The University of Alberta
Printing Department
Edmonton, Alberta

THE UNIVERSITY OF ALBERTA

A LABORATORY EVALUATION OF THE USE OF ACTIVATED CARBON FOR THE DETECTION OF THE TRACER DYE RHODAMINE WT

by

© PETER LYNN SMART

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF GEOGRAPHY

EDMONTON, ALBERTA

FALL, 1972.

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled A laboratory Evaluation of the use of Activated Carbon for the Detection of the Tracer Dye Rhodamine WT, submitted by Peter Lynn Smart in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

The nature of activated carbon is discussed with reference to preparation, physical and chemical structure. Rhodamine WT is described. It is unstable below pH 6.0 and sensitive to Cl^- at concentrations of 0.01M.

Carbon capacity is dependant on particle size and solution concentration, but independant of pH and ionic strength. Adsorption rate is dependant on solution concentration, unused carbon capacity and particle size. In fresh waters variations of pH and ionic strength do not cause significant changes in adsorption rate, however larger variations are important. Competition from dissolved organic matter reduces capacity and adsorption rate compared to those in distilled water, the amount of change being dependant on flow rate, time and organic concentration. Desorption of adsorbed dye can occur until a loading at which solution equilibrium concentration is zero. It is concluded van der Waals forces are responsible for adsorption, with a small contribution from hydrogen bonding.

The higher the ratio of elutant volume to carbon weight, the larger the elutant fluorescence, and the faster this maximum was achieved. Large unbranched alcohols were better elutants than the smaller more polar members, though an increase in the water content of the elutant was necessary for the former. Ammonium hydroxide additive caused release of additional dye, and also stabilised fluorescence. Increase in elutant temperature produced increased desorption, but the effect was masked if a temperature correction was not applied. The

evidence indicated that competition by the alcohol molecules, adsorbed by van der Waals forces, was primarily responsible for desorption, though some release from polar sites was achieved by the use of ammonium hydroxide.

The amount of dye released on elution was dependant on elutant, temperature, dye loading on the carbon, initial solution concentration and the length of time since adsorption occurred. The column system would give more dye release than the batch system. The Soxhlet extraction apparatus would be the best apparatus for elution. Recommendations from these laboratory findings for application of the method in the field are given. It is concluded that simple quantitative interpretation of carbon adsorption/desorption data is not possible.

ACKNOWLEDGEMENTS

I would like to thank the Department of Geography, University of Alberta, and Dr. M.C. Brown for financial support during this study. I would also like to thank Charlie Brown for being an extremely approachable and helpful supervisor. Dr. Ian Drummond has given useful discussion on several technical topics, and also helped to determine the pK_A of Rhodamine WT; the ideas expressed herein are nevertheless solely those of the Author. The diagrams were prepared by Mrs. Stephanie Kucharyshyn to whom I am very grateful. Much of the experimental work was aided by my wife, Margaret, who is also responsible for all the typing.

Table of Contents

List of Tables

List of Figures

I INTRODUCTION

Fluorescent dyes have been widely employed as tracers in all portions of the hydrologic system since their introduction for use in surface waters in the early 1960's by Pritchard and Carpenter (1960), Feuerstein and Selleck (1963a), Wright and Collings (1964), Buchanan (1964), Watt (1965), Cobb and Bailey (1965), Replogle et al (1966) and more recently Wilson (1968a and 1968b), various authors in Water Supply Paper no. 1892 (1968) and Kilpatrick (1970). The superior properties of the xanthene group, and in particular Rhodamine WT, a dye developed specifically as a water tracer by Du Pont de Nemours & Co. (U.S. Patent 3367946 1968) have caused many workers to adopt these dyes. However the fugitive dye uranin (sodium fluorescein C.I. 45350) had previously been widely applied in groundwater tracing, especially in karsted aquifers, where it was generally found satisfactory (Dole 1906, Ambrose 1921, Plummer 1945, Sturm and Johnson 1950, Heck 1954, Kaufman and Orlob 1956, Haas 1959 and many others). Rhodamine WT was also used in groundwater studies after its introduction because of its desirable properties and associated developed quantitative technology (Scanlan 1968, Brown, Ford and Wigley 1969, Aley 1971, Brown in press). Due to the high natural background fluorescence at a wavelength corresponding to the fluorescence maximum of sodium fluorescein, quantitative determination was limited to higher, undesirable concentrations (Feuerstein and Selleck 1963, Watt 1965, Knochenmus 1967, Scanlan 1968). However its use has continued where qualitative information only is required, due to its cheapness and the

considerable expertise which has been built up on its use (Zotter 1963, Baucic 1965, Bidovec 1965, Molitvin 1966, White 1967, Käss 1967, Knutsson 1968, Scanlan 1968, Aley 1971 and many others).

Dunn (1957) first introduced a carbon detector system in order to facilitate groundwater tests in which the destination and time of travel of water tagged with fluorescein were not known - the normal case in karst groundwater systems. Activated cocoanut carbon, placed in a pipe sealed by wire mesh at both ends, was used to adsorb dye passing the detector site. After collection the dye was eluted from the carbon using 5% potassium hydroxide solution in ethyl alcohol. The presence of fluorescein, detected visually, in the elutant indicated a successful trace from the input site to the detector.

The method was generally adopted by workers in karst areas and developed in an empirical manner. The detector construction was improved by employing an all wire mesh packet (Haas 1959), while other workers suggested that nylon stocking mesh bags were satisfactory (Zotter 1963, Drew and Smith 1969). Suggestions about the effects of drying the carbon after collection (Zotter 1963, Aley 1971), the effect of flow (Aley 1971, Scanlan 1968) and of the frequency of changing the detectors (Haas 1959, Drew 1968, Drew and Smith 1969, Aley 1971) were made as experience was gained with the method. Various elutant compositions were also tried (Zotter 1963, Scanlan 1968, Drew and Smith 1969, Aley 1971) and other dyes employed (Scanlan 1968, Drew 1968a, Drew and Smith 1969, Aley 1971). However only Scanlan has presented any specific scientific experiments which were designed to optimise the method. All other improvements have been presented as being the results of experience using the method, and are unsupported by data from which their effectiveness may be evaluated

by other workers. Unfortunately Scanlan's work is rather limited in scope and may be criticised on several methodological points. There appears to be little or no understanding of the theory or mechanisms of adsorption on, and elution from carbon.

Thus, although these methods have been widely demonstrated to work satisfactorily there is little or no information available on the effects of specific variables on their performance. Furthermore it is not known if the methods employed are the optimum for the system, or if they may be improved by the use of other specific carbons, adsorption or elution conditions, or elutants. This is of considerable importance in that the method can only be used to demonstrate positive traces; negative results may be attributed equally readily to poor technique or to the hydrologic system under investigation (Classen 1967). By optimising the method it may be possible to lower the detection threshold of the system and hence allow borderline tests to yield useful information.

Previous use of the detector has been in the determination of point to point flows with, in some cases, an approximate assessment of flow-through time due to periodic replacement of the detectors (White and Schmidt 1966). However with the development of water budget techniques based on flow-net theories and dye dilution gauging for discharge measurement, quantitative information is needed (Brown and Wigley 1969, Brown, Ford and Wigley 1969, Brown and Ford 1971). In particular, if an activated carbon system could be used to measure the mass of dye emerging at a given point, a simple discharge measurement would allow the flow-net theory to be used without continuous monitoring. Further refinements might allow information on travel time and perhaps pulse duration to be obtained.

The practical necessity for remote detection of dye pulses in groundwater traces has not changed. Furthermore, the extension of tracing work, from the large relatively accessible sink to rising and vadose zone streams of maturely karsted aquifers, to soil and percolation waters (Drew 1968a) and to diffuse flow systems, demands that techniques for remote sensing of tracers in inaccessible locations be improved. As activated carbon provides a cheap and relatively efficient method for monitoring dyes, and is extremely simple to operate, it may provide a satisfactory tool for use in such situations.

Thus the purpose of this study may be stated as follows:-

1) To apply and optimise the use of the activated carbon detector technique for the tracer dye Rhodamine WT.

2) To provide an explanation of the mechanisms operative in the adsorption/elution of Rhodamine WT on activated carbon, and evaluate the specific factors affecting it, such that other workers may further develop the technique.

3) To assess the applicability of activated carbon for possible quantitative determination of Rhodamine WT.

No attempts have been made to evaluate the techniques in field situations; this study has concentrated wholly on a laboratory evaluation in order to provide a sound basis for future development of practical applications.

1. Activated Carbon

In order to effectively utilise activated carbon it is necessary to understand how and from what it is prepared, and what desirable properties this preparation imparts to raw material. Such an understanding

has been generally lacking in users of the carbon detector method and has greatly hindered proper application of this material.

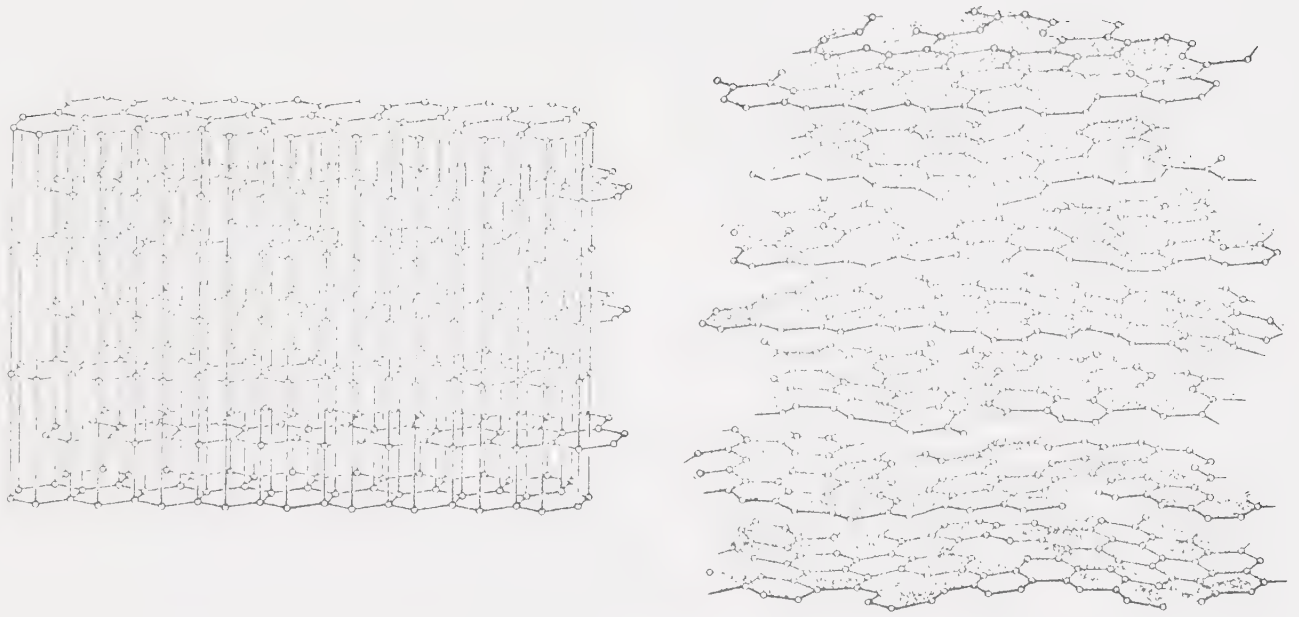
There are two basic methods of carbon preparation; physical and chemical. In the physical process a carbonaceous material (cocoanut shells, peat, coal, bone char, sawdust, lignin and many others) is carbonised by heating. Much of the non carbon material is burnt off leaving free carbon atoms, which combine to form graphitic crystallites. The areas between these fill with amorphous carbon and tars; the activation process removes this material to leave a highly porous, microcrystallite based, carbon solid. Activation is usually carried out by burning with an activating agent, normally chlorine, steam,carbon dioxide or other oxidising gases. The longer activation continues, the greater the number of large pores which are produced relative to smaller ones. This process is commonly used for decolourising carbons. The chemical process involves only one step, and is normally used to produce microporous gas adsorbent carbons. A tar formation inhibitor, for example zinc chloride, is added to the carbon and a porous solid produced in a single step.

Thus activation is marked primarily by an enormous increase in pore size. Carbon cannot become "deactivated" during use; it merely becomes spent as the adsorption capacity is reached (cf Williams, in Drew 1968). By varying the temperature, time and oxidising materials used in activation, and the additives and starting material, different desirable properties may be obtained. For instance, cocoanut carbon is resistant to attrition and has a highly microporous structure. Smišek and Černý (1970 ch.2) and Hassler (1963) present accounts of carbon preparation.

The basic structural unit of activated carbon is the microcrystallite. This is composed of graphite-like layers 20 to 50A in diameter

Fig. I:1 Schematic Diagram of Graphitic and Turbostratic Structures

Source: Weber et al (1970)



A. Three Dimensional Graphite Lattice

B. Turbostratic Carbon Structure

stacked one above the other to produce a thickness from 20 to 100A. In the perfect graphite structure, carbon atoms are arranged in complete aromatic rings stacked such that alternate layers are directly above each other. Layer separation is 3.35A (Fig. I:1A). In activated carbon, however, this regular structure is not present: the aromatic layer is buckled and has many bond defects where carbon atoms are missing, separation distance increases to 3.6A, and the alternating structure is completely absent, each layer being randomly orientated with its neighbours. This is known as turbostratic structure (Fig. I:1B). It is due primarily to the presence of strong bonds, from holes and other defects in the aromatic structure, and particularly from the layer edges, which link neighbouring layers and microcrystallites and prevent proper orientation from being adopted. Thus the structure might rather be modelled by a complex organic polymer than by a perfect graphite structure.

The microcrystallites are grouped into regions which have similar flat orientation of the turbostratic layers in neighbouring microcrystallites. The larger pores in the structure, formed by burn off of reactive hydrocarbon radicals at the microcrystallite edges, are known as macropores, and have diameters of 200 to 1,000,000A. These provide the primary routes for transport to the extensive internal surface which is characteristic of activated carbons. Surface areas normally range from 500 to 2000m^2/g, most of which is provided by the micropores. The latter are formed by burnout of whole microcrystallite planes and defects in the carbon layers. They have diameters from 4 to 10A and provide the most important source of adsorption sites. A further pore size from 10 to 200A is known as transitional porosity, and is developed when prolonged activation is employed to burn out a large number of micropores. It is

particularly important for adsorption of large molecules, which experience molecular sieve effects in the micropores.

The basic chemical structure of activated carbon has been shown to be that of a complex partially aromatic organic polymer. Two types of chemical sites are recognised in this structure: firstly, highly reactive ones, present at defects in the microcrystallite layers and at their edges; and, secondly, the unreactive basal (aromatic) portions of the layers. The latter are relatively uniform with few attached functional groups, due to the lack of suitable bonding sites. Sorptive processes on these surfaces are dominated by van der Waals forces and electron donor/acceptor complex formation utilising the aromatic π electrons. The second series of sites are normally occupied by attached functional groups, chiefly oxides and hydrocarbon complexes. They provide important sites for specific bonding by ion exchange and coulombic forces, and also stabilise the carbon structure by inter-layer crystallite bonding.

Oxygen may comprise 2 to 25% by weight of activated carbon and hydrogen from 8 to 19 times that of oxygen on a molar basis. The magnitude of these non carbon constituents indicates that a great number of surface functional groups must be present. Considerable work has been carried out to identify the nature of these groups by indirect methods (see review by Boehm (1966)) and recently by more direct methods (see Mattson and Mark (1971)). It is sufficient for this study to note that four types of acidic groups are normally recognised: a strongly acidic carboxyl group (capable of lactone formation), a more weakly acidic carboxyl group, a phenolic hydroxyl group, and a carbonyl group; while only one basic group has been tentatively suggested, a chromene group capable of forming a carbonium ion (Garten and Weiss 1957).

The information for the above discussion was drawn from Garten and Weiss (1957a), Hassler (1963), Boehm (1960), Weber (1967), Snoeyink and Weber (1967), Coughlin (1969), Smišek and Černý (1970) and Mattson and Mark (1971). These references should be consulted for further information on this topic.

The activated carbon used in this study was obtained from Fisher Scientific Co. (Cat. 5-685). It was described as being primarily for recovery of oils and solvents from the vapour phase, and not for decolourising; however it was used because it was resistant to attrition, had a particle distribution (Table I:1) suitable for practical application and had previously been used in the field. The special decolourising carbon supplied by Fisher (Cat. 5-690) was far too fine. No reply

Table I:1 Particle Size Distribution of the Experimental Carbon

Particle Size (mm)	Percentage Greater than Size (%)
3.36	0.0
2.86	15.2
2.38	42.5
2.00	63.0
1.68	83.0
1.41	93.7
1.19	98.7
1.00	99.6

(By sieving)

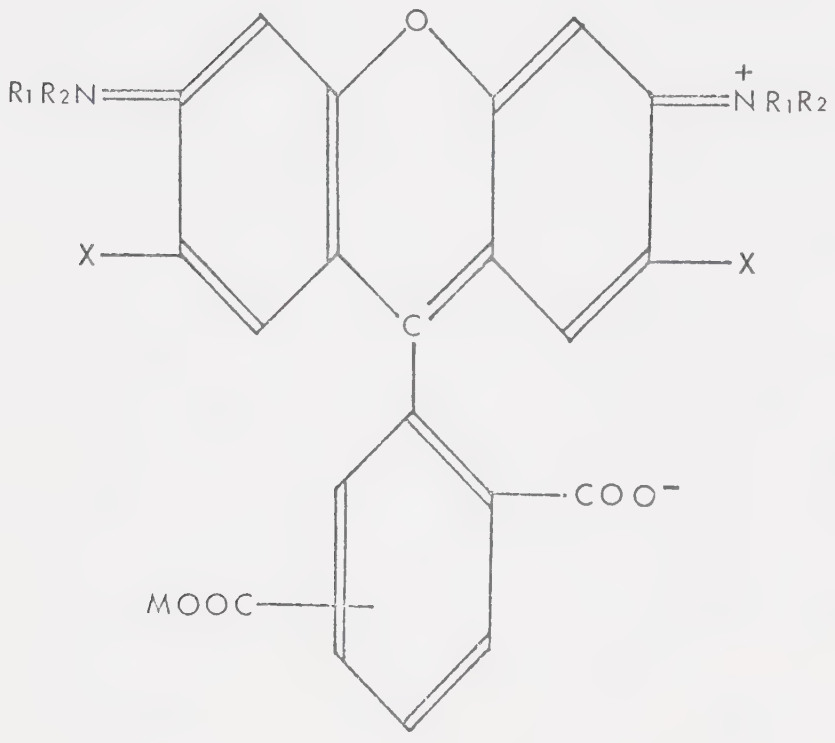
has been received from the supplier after a request for information on the properties, preparation and raw material of this carbon.

2. Rhodamine WT

Rhodamine WT is a xanthene dye of the rhodamine sub-group, which

Fig. I:2 Structure of Rhodamine WT

Source: U.S. Patent 3367946 (1968)



Where: R_1 is C_{1-4} alkyl; R_2 is H or C_{1-4} alkyl; X is H, or is CH_3 when R_2 is H; M is H, Li, Na, K or $H\text{-}NR_3R_4R_5$ where R_3, R_4 and R_5 separately represent H, C_{1-4} alkyl, alkanol having 2 to 4 carbon atoms, or R_3, R_4 and R_5 together with the nitrogen atom represent a monocyclic hetero ring.

It may be suggested that a likely possible structure for the dye would be: R_1 is C_1 alkyl, R_2 is H, X is C_1 alkyl and M is H, when the dye is protonated, or Na for the dye salt - the dye then probably being in sodium hydroxide solution.

was introduced by Du Pont de Nemours and Co., the manufacturers, in 1964 as a less costly substitute for Pontacyl Brilliant Pink B; both exhibited better resistance to adsorption than rhodamine B. Rhodamine WT is the subject of U.S. Patent 3367946 (1968), which is the only published information describing the dye. Unfortunately a specific description is not given, as the patent is for the general class of dyes. Requests for more detailed information have been politely refused by the manufacturers.

The dye (Fig. I:2) is a zwitterion, but is anionic (acid) in character. It comprises three substituted benzene rings, connected by a xanthene ring, and is normally in the quinonoid form, though it appears that under acid conditions it may revert to a lactone form. It is supplied as an alkaline aqueous solution, but may be obtained as a solid by evaporation to dryness. The concentration of the solution is adjusted with reference to a standard solution of rhodamine B to an accuracy of $\pm$ 19%. As no attempt was made to determine absolute concentration in this study, the absolute values reported should be used with this tolerance in mind. A single batch of dye was utilised throughout these experiments. It is obviously important to recalibrate the fluorometer for each dye batch when carrying out quantitative work in the field, in that a given calculated concentration may produce completely different fluorescence readings.

A Turner III fluorometer with Turner filters #110-832 (primary) and # 110-833 (secondary) was employed to determine dye fluorescence, which was converted to concentration employing prepared calibration curves. All readings were corrected to 21°C by measuring cuvette temperature with a YSI thermister, and using Wilson's correction curve for Rhodamine WT. Wilson (1968a) has discussed fluorometric determination of

dyes using this instrumentation very completely in a monograph from which detailed information may be obtained.

Although the machine functioned reasonably well over the period of experimentation, several problems were noted. During the initial phase of the study it was found that the calibration curve changed erratically from day to day. This was finally attributed to a faulty lamp (General Purpose UV #110-850) which was changed to give more stable readings. However, over long, but non continuous, periods of operation there was a gradual drift in calibration and sometimes jumps, which could not be attributed to any specific malfunction. It was probably due to aging of the lamp, and perhaps detection system, in the fluorometer. A correction was made by periodic recalibration and use of freshly prepared standards to produce a correction factor (correct concentration = concentration read X [calibrated concentration of standard / concentration of standard read]).

It was also observed that the scale changing assembly was not completely accurate. By pressing the knob to the left, after location in a given scale slot, a reading different by 6 to 7% of the average from a value for the same sample determined with the screen to the right was obtained. This was compensated for by calibrating and using the fluorometer with the scale knob firmly to the right of the slot. This problem must be common to all Turner III fluorometers, but has not previously been reported. Some wear was also noted in this scale changing assembly, and it appears that a non-fluorescent lubricant should be used, if possible, to reduce this.

II ADSORPTION

1. Introduction

There appears to be no information in the literature on the carbon detector method dealing with adsorption. The approach adopted is that adsorption of the dye does occur and it is therefore unnecessary to know the systematic variables controlling adsorption, or its mechanism. This situation is unsatisfactory in that where negative test results are obtained, methodological inadequacies may be responsible rather than the failure of a dye pulse to pass the detector.

Three dependant variables are important in the operation of the carbon detector method: the capacity of the detector for dye, the kinetics of adsorption of dye on the detector, and the degree of reversibility of the adsorption process. It is necessary to determine the effect of both charcoal/dye interaction and environmental controls on these dependant variables. Thus the effect of dye concentration, carbon weight, dye loading, carbon type and carbon size were assessed for the former group above, and pH, ionic strength and temperature for the latter. These variables have all been found important for other aqueous organic solute/activated carbon systems. In addition experiments were conducted to assess reversibility, and determine the significance of aging of carbon in both air and water. From the results of this work it was possible to discuss adsorption mechanisms and hence produce explanations for the effects of the systematic variables investigated.

It is generally recognised that the best extraction system, when considering effectiveness of removal and efficiency in utilisation of

the carbon, is the column system, in which the fluid is passed through a column of adsorbate (Weber and Morris 1963a and 1964b). The detector system approximates this mode of operation, except that flow may be three-dimensional and the column is of extremely short length. It would therefore be most satisfactory to use experimental techniques which model this flow-through system, as was in fact employed by Scanlan (1968). However the column system has many disadvantages from the experimental point of view and the batch system, in which a known weight of carbon is contacted with a given volume of dye solution of known concentration in a closed system, is more generally used.

In this study the batch system has been employed. It has the advantages of experimental simplicity, good reproducibility, lack of complex experimental equipment and freedom from complex hydraulic parameters indigenous to flow-through systems (Weber and Morris 1963a and Hassler 1963). Furthermore the results of such investigations are readily transferable to the column mode in terms of capacity using such approaches as the LUB/equilibrium section concept (Collins 1967). However, as Smith et al (1959) point out, rate data is considerably more difficult to transfer and must very often be determined empirically once the column has been constructed. This problem is not of importance in this study as it is not necessary to know absolute adsorption rates for the detector "columns"; of more importance is the effect of systematic variables on the relative adsorption rates for a given batch system.

Another choice in experimental methodology is that between constant and variable concentration batch methods. In the former, solution concentration is maintained by additions of solute as adsorption occurs, while in the latter no dye is added after the initial amount and solution

concentration decreases to an equilibrium. The latter method is more widely used, is simpler, and fits more readily into the theoretical adsorption models which have been proposed. Peterson and Lee (1971) provide a comparison of the two methods for adsorption of rhodamine B on activated carbon. The constant concentration equilibrium loading values are lower than those for the ordinary batch method, probably because higher initial concentrations are used in the latter.

Data from batch adsorption experiments is normally presented as an adsorption isotherm, defined as the relationship between the quantity of solute adsorbed per unit weight of adsorbate and the equilibrium concentration of the solute in solution at a given temperature (Graham 1959). This representation is adopted herein. Several models have been proposed to explain various common forms exhibited by the adsorption isotherms, but none proved satisfactory to describe the data obtained in this study. Details on the application, derivation, and limitations of these models may be obtained from Graham (1959), Hassler (1963), Kipling (1965), Maron and Prutton (1965), Weber and Morris (1964b) and Weber (1967) or other standard physical chemistry texts.

In all adsorption experiments reported in this study, standard batch adsorption procedures have been followed. The carbon sample was washed in distilled water to remove dust, dried in thin layers at 115°C in a natural convection oven and homogenised. The desired weight was then weighed out into a wide mouthed 250ml Pyrex-glass conical flask. A known volume, not exceeding 200ml, of prepared dye solution of a given concentration and chemical composition was then transferred into the flask, which was sealed with a rubber stopper. Dye concentration and charcoal weight were varied in order to provide a range of points to

allow construction of the appropriate adsorption isotherm. The time was noted and the flask placed on a New Brunswick Scientific Company oscillating shaker running at 260 revolutions per minute, in a light-proof enclosure the temperature of which was kept at 23°C $\pm$ 1°C. After an appropriate time period the flask was removed, and a 10ml aliquot of the solution pipetted into a 15ml centrifuge tube. This was stoppered and centrifuged on an international Model CL centrifuge at setting seven for 6 minutes. (This was found to be sufficient in preliminary experiments to remove all carbon particles from the solution). The sample was removed and 5ml carefully transferred into a selected Pyrex-glass cuvette. The fluorescence was determined using the Turner III fluorometer and sample temperature was taken using a YSI thermister to allow correction for variation of fluorescence with temperature. The sample was returned to the centrifuge tube, which was shaken to resuspend carbon particles, its contents were then returned to the conical flask to avoid volume or carbon loss. The flask was returned to the stirrer and agitated again until a further sample was needed. Sampling was ceased when equilibrium values of solution concentration were obtained. A blank was run to allow estimation of apparent dye adsorption due to loss on glassware, oxidation or other non-adsorptive losses.

It was found that some attrition of the carbon samples occurred due to the high stirrer speed utilised, but unfortunately no other suitable apparatus was available. For several runs, times to equilibrium were excessive and samples were removed when the rate of decrease of solution concentration was less than three scale divisions per three day period. This is theoretically unsatisfactory as it confuses rate and capacity information but was a practical necessity when times in excess

of 1000hrs occurred. It has been commonly used in several published studies e.g. Hassler and McMinn (1945). It was found that a drift in the fluorometer calibration curves was often evident over the period of study and hence, where appropriate, a correction factor was employed using a non-agitated standard solution. The concentration determined for the standard at a given time was subtracted from the concentration on calibration, and the percentage change calculated. This percentage was then employed to correct all other readings. The technique assumes linear calibration curves, as are normally obtained in fluorometric analysis (Wilson 1968a).

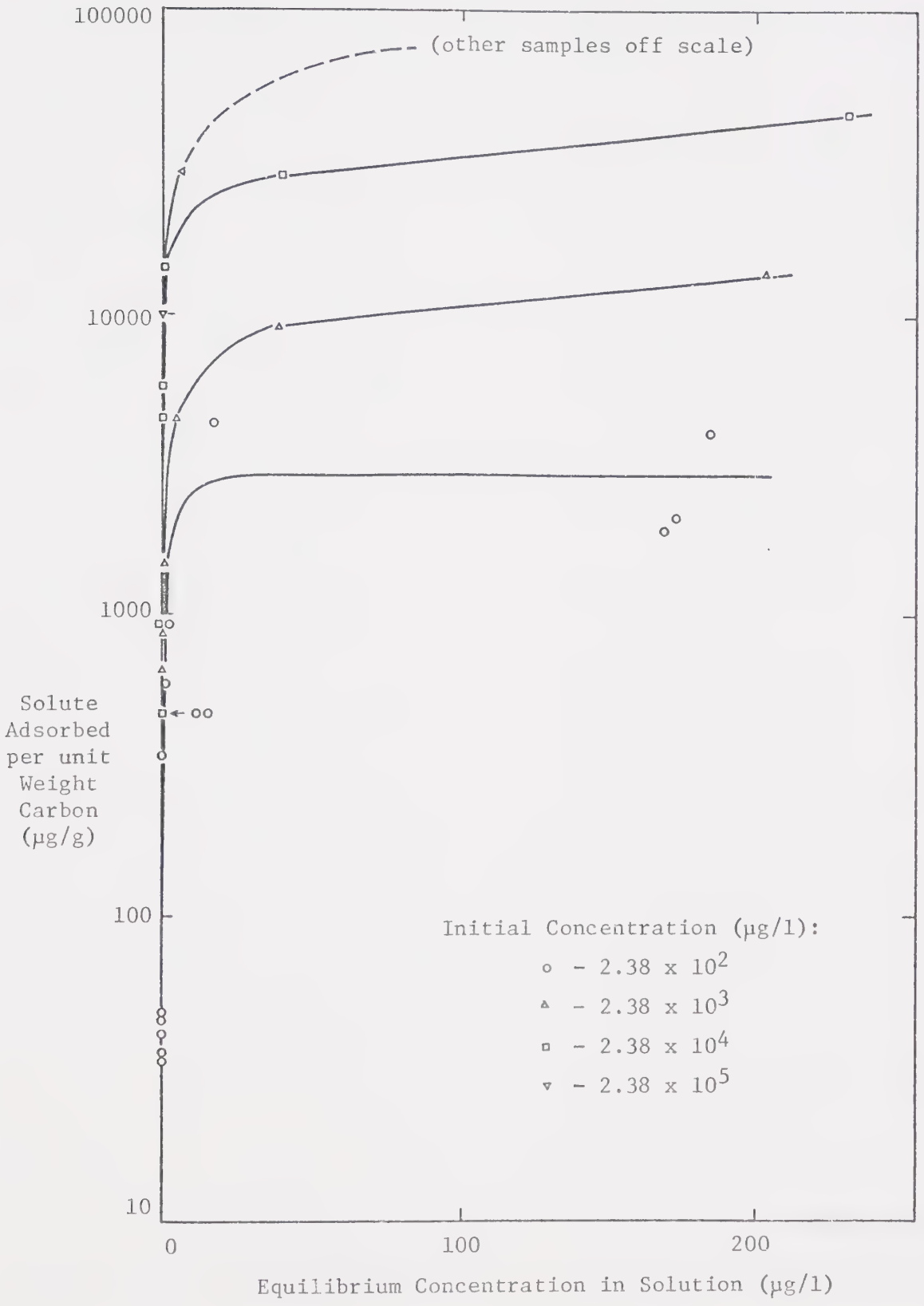
2. Dye/Carbon Interaction Effects

A. Capacity

The adsorption isotherms determined using the standard activated carbon without further treatment were found to be very irregular. Further analysis showed that this effect was due mainly to changes in the initial concentration of the solution. Fig. II:1 presents isotherms for which initial solution concentration was varied over four orders of magnitude. Attempts to apply the Langmuir and Freundlich equations to the data produced a poor fit. The isotherms appear to indicate that after some monolayer or equivalent coverage is achieved, represented by the marked knee, there is further adsorption, which in gas adsorption would correspond to formation of multilayers. Unfortunately the saturation concentration of Rhodamine WT was not available, precluding application of the B.E.T. equation, which would be expected to fit this isotherm type.

There is a marked increase in the monolayer value, represented by

Fig. II:1 Effect of Initial Concentration on Adsorption Capacity of Carbon



the knee, and also an increase in the gradient of the isotherm after this point with increasing initial concentration. These findings were supported by data from a sorted carbon (0.46mm), which is not presented. Velasco and Ruiz (1945 and 1948) report identical isotherm forms for a variety of dyes on activated carbon, as do Galbraith et al (1958) for adsorption on graphite. Velasco and Ruiz (1948) also observed that different Freundlich isotherms were produced if initial concentration was varied and recommended using a constant concentration with varying volume or adsorbent weight. Weber and Morris (1964b) report an identical concentration effect to that noted here for phenol on activated carbon.

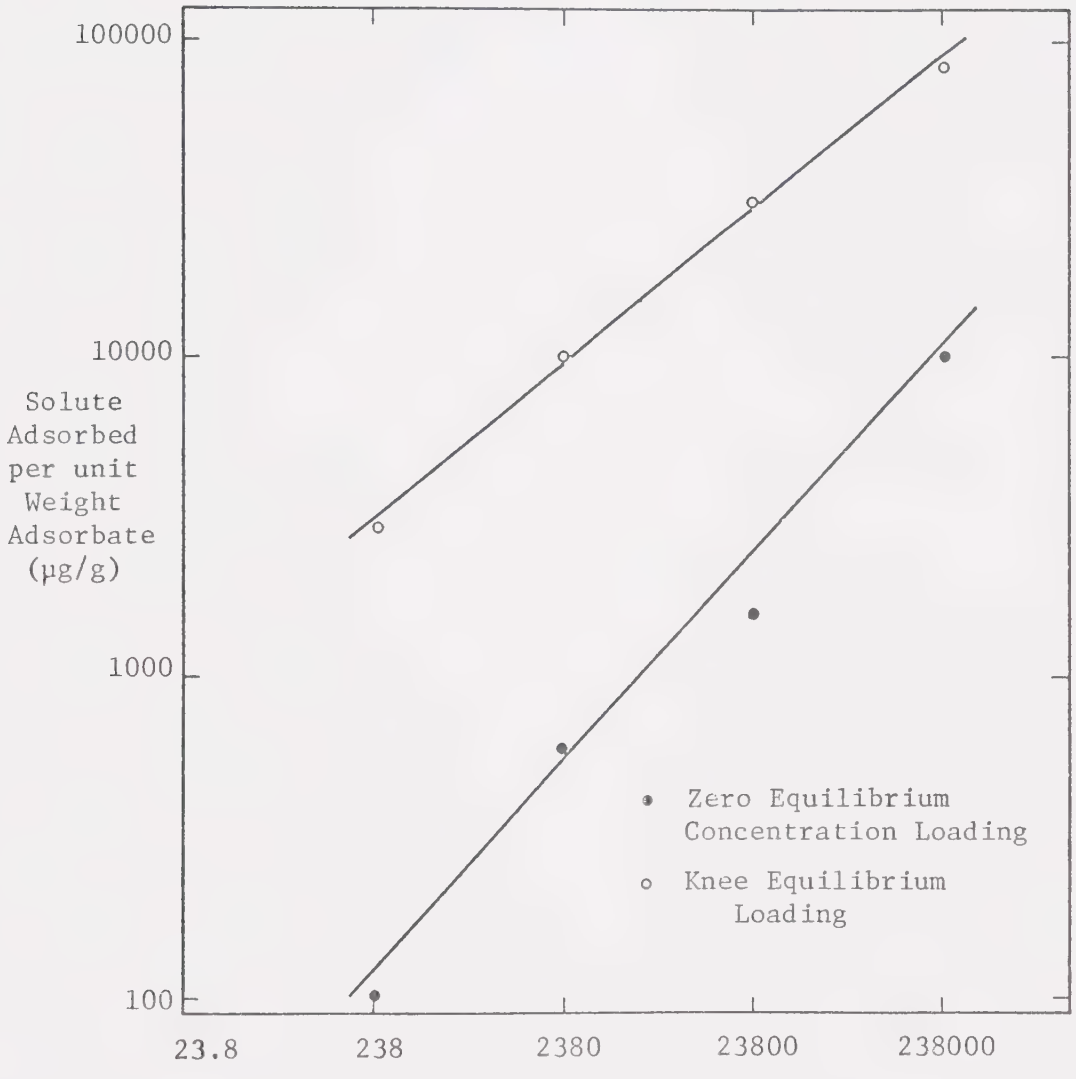
The L shaped isotherm found in this study indicates that adsorption is probably either as a monolayer of small ionic micelles or of monodisperse dye molecules (Giles et al 1964). More recent work by Giles (Giles and D'Silva 1969) has shown that, for dye adsorption which is controlled primarily by physical forces e.g. van der Waals dispersion forces compared to covalent bond formation, an initial monolayer of monodisperse ions is formed. On increasing the solution concentration these ions form the nucleus for the development of small ionic micelles which increase in number until no further micelles can form at that concentration and an asymptote is caused in the isotherm. Unless specific bonding to the surface dominates adsorption, the micelles are adsorbed parallel to the surface with the planar aromatic molecules stacked flat one above each other, as in a deck of cards (Giles et al 1966). This stack structure is a result of the maximum effectiveness of van der Waals forces when separation distances are minimised (Bergmann and O'Konski 1963), and in the case of Rhodamine WT probably also due to micelle stabilisation by the zwitterion charges (Galbraith et al 1958). The former is probably

also responsible for planar orientation on the surface (see below p34 where the mechanism of the adsorption bond is discussed).

The observation of non-integer aggregation numbers on several adsorbate surfaces indicates that a variety of micelles containing different numbers of molecules occur on adsorption (Giles et al 1966 and Giles and D'Silva 1969). As concentration increases there is a proportional increase in the number of large micelles both in solution and on the substrate. The concentration effects observed are due to this increase. Hence at equilibrium, increase in the solution concentration will cause the number of large micelles to increase on the surface. Thus more molecules are adsorbed onto the carbon, the bonding forces being those of micelle formation rather than adsorption. This explains the non-zero isotherm gradient after the knee. A somewhat similar explanation was used by Velasco and Ruiz (1948), though they referred to physical adsorption to produce a monolayer, followed by capillary condensation without mentioning micelle formation. The forces for capillary condensation are similar to those of micelle formation.

Similarly the increase in amount adsorbed with increasing initial concentration is due to the formation of large micelles at the carbon surface due to high concentration. These occupy identical sites at the surface to the smaller micelles formed at lower initial concentrations, hence giving higher loading per site, though some molecular sieve activity will be present in the micropores (Giles and D'Silva 1969a). It is because larger numbers of big micelles form at high concentrations than at lower ones, that there is an increase in the "monolayer" coverage with initial concentration. Fig. II:2 shows the decrease in equilibrium and zero-equilibrium-concentration capacities with initial concentration.

Fig. II:2 Relation Between Initial Concentration and Carbon Loading

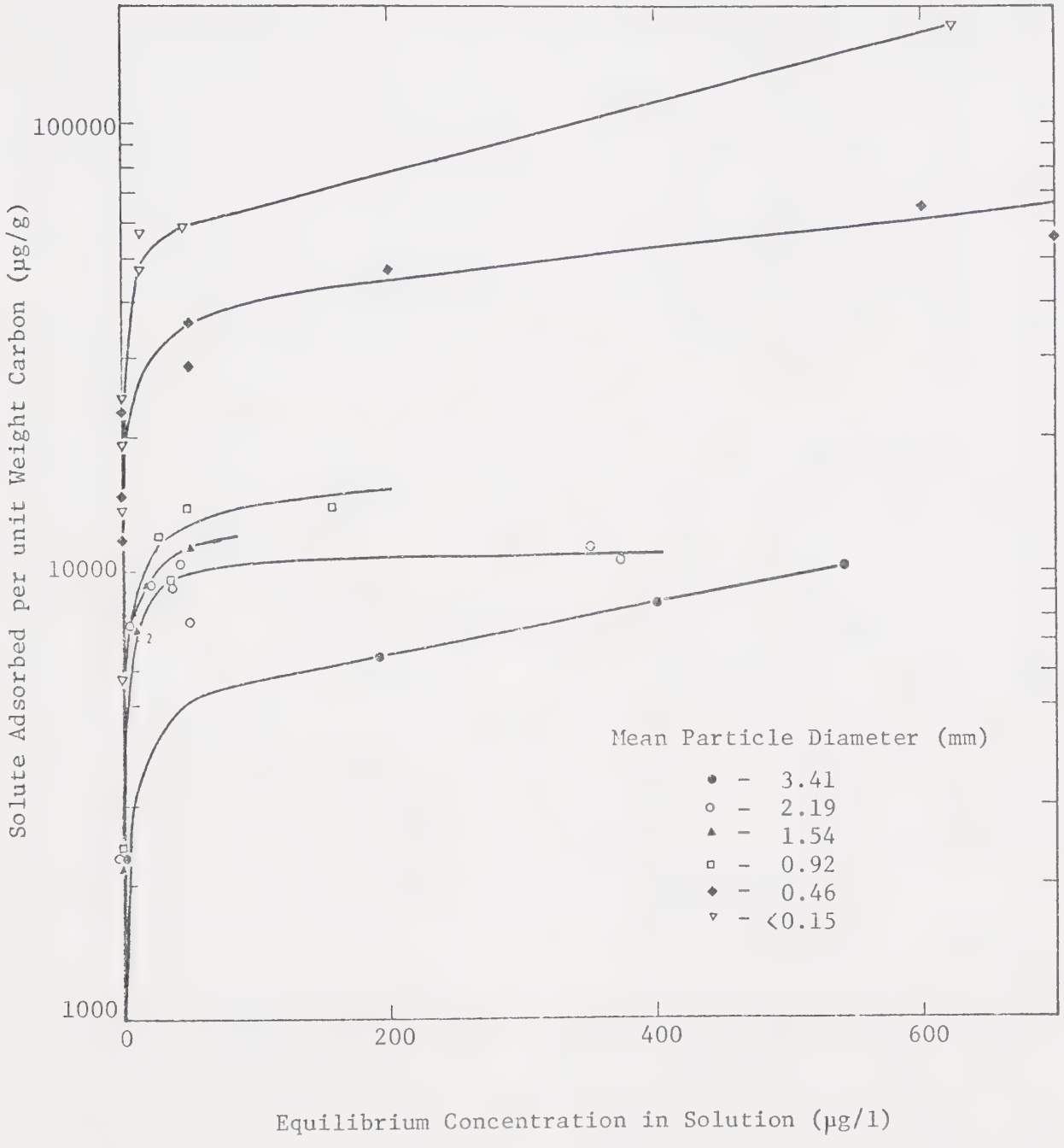


The relation is linear for a log/log plot. Extension indicates that low loadings would be given by the concentrations normally used in tracer tests, especially if desorption is allowed to occur after adsorption (see below p35).

Further irregularity in the isotherms was due to the heterogeneity of the carbon used with reference to particle size. This was particularly so in the low concentration isotherms where small carbon dosages prevented the use of a sufficient number of grains to produce a reasonable approximation to the particle size distribution in bulk. The bulk carbon was seived into a number of particle sizes using a fifteen minute shaking period. Finer sizes were produced by hand grinding in a pestal and mortar, as the yield from sieving alone was low. Average particle sizes of 3.41, 2.19, 1.54, 0.92, 0.46 and less than 0.15mm were used, and adsorption isotherms determined using initial dye concentrations of 2.38×10^3 to 9.52×10^3 µg/l.

The isotherms produced are shown in Fig. II:3. There is a marked increase in equilibrium capacity with particle size for the isotherm knee. Furthermore the average particle size (2.19mm) shows agreement with the isotherm for this initial concentration using unsorted carbon, indicating that the latter was produced from carbon samples having a satisfactory particle distribution. The findings from this study comply with those from other work (Weber and Morris 1964a and 1964b, Weber 1967). However, the empirical relationship between capacity and the reciprocal of the diameter squared noted by Weber and Morris (1964b) was not followed. The large separation of the 0.92mm and 0.46mm isotherms, compared to that between 0.46mm and less than 0.15mm, may be due to the grinding used to produce these finer grain sizes (Hassler and McMinn 1945).

Fig. II:3 Effect of Particle Diameter on Equilibrium Capacity



During the formation of smaller granules by fracturing of larger ones, closed and "ink-bottle" pores are opened to allow solute penetration and hence a larger accessible surface (Weber 1967, Weber and Morris 1964b). This increase in surface area may also be augmented by the increase in external surface per unit weight as particle size is decreased, though this cause is probably minor compared to the former. Although Davies (1968) does not agree with this explanation, Mattson and Mark (1971 p203) have shown by nitrogen/BET surface area measurements that crushing does produce a considerable increase in accessible surface.

In practical situations higher capacities may be obtained using smaller carbon particle sizes. However, the flow restrictions caused by the small particles and the finer envelope material needed to contain them are probably of more significance than this relatively small gain in capacity. It is important in using the isotherm capacity data presented to evaluate the amount of carbon to be used in a detector, to remember that the values presented are based on achievement of equilibrium. In practice there is an interaction of rate and capacity terms to produce an effective capacity after an adsorption period of a given time. Furthermore, the knee capacity data represents an equilibrium capacity far higher than practically possible, as concentrations were at least an order of magnitude greater at this point than in field operation.

B. Rate of Adsorption

The expression of rate data in adsorption studies is rather difficult, and has generally been ignored, the emphasis being placed upon equilibrium capacity, rather than kinetics. Various techniques were used to describe the data from this study, but none were wholly

satisfactory. Vickerstaff (1954 p148) recommended a hyperbolic function to describe the time/concentration curves, but this was found to give a poor fit. Similarly Weber and Morris' (1963a) linearisation employing a $t^{0.5}$ transform of the time axis fitted only the first few hours of the adsorption process, which continued in many cases for over 1000hrs. Other more complex expressions proposed by Smith et al (1959), Cookson (1969) and Lindstrom et al (1970) were discarded either due to a poor fit or lack of the appropriate data.

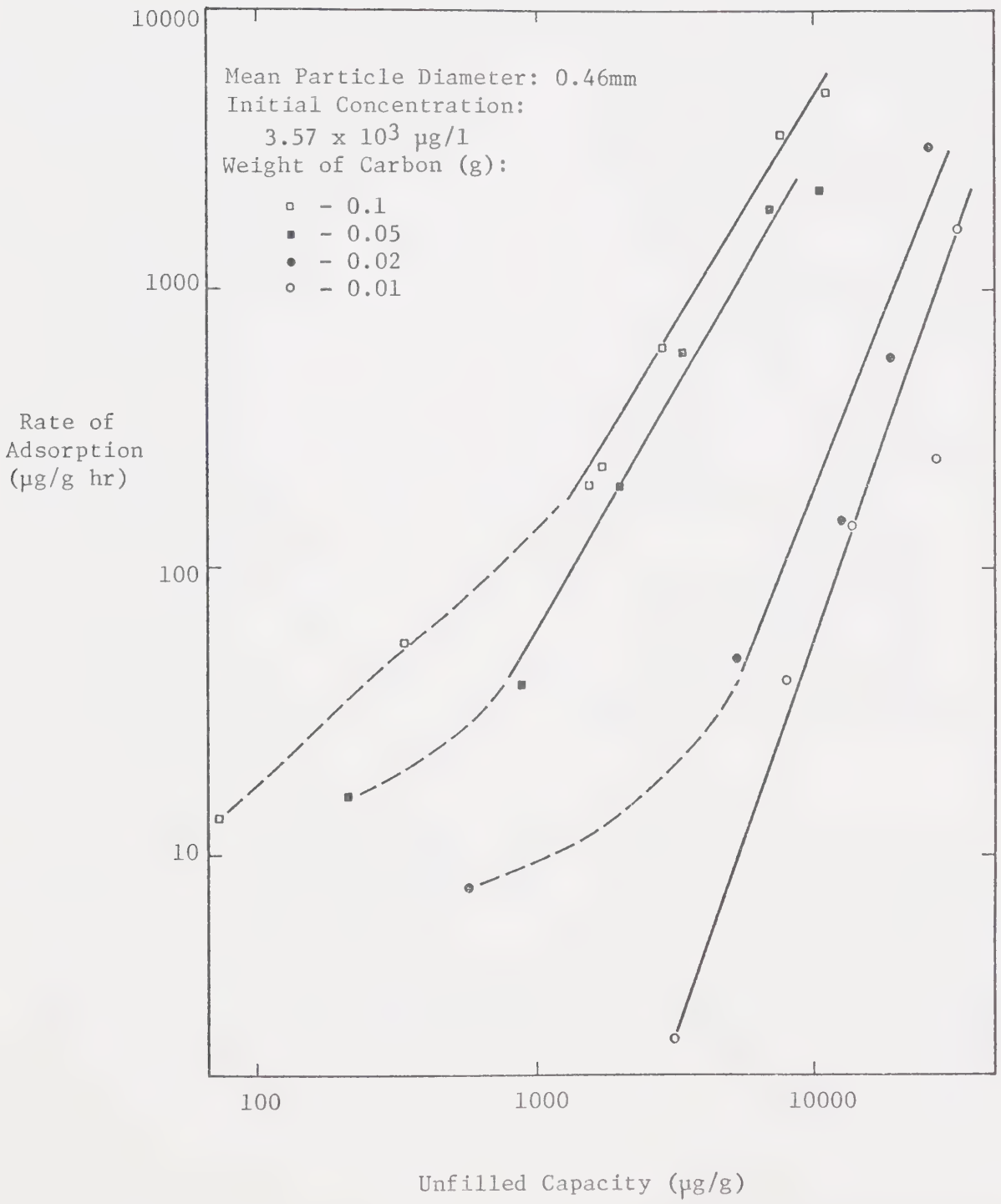
The representation finally adopted was devised empirically by Swearingen and Dickenson (1932) and is an exponential equation of the form:-

$$C_t = C_\infty + e^{-kt}$$

where C_t represents concentration at time t, C_∞ is concentration at equilibrium and k is a rate constant (for constant volume, concentration may be replaced by amount adsorbed per unit weight of adsorbate). This equation may be linearised by taking the logarithm of $C_t - C_\infty$ and plotting against t. Another convenient plot is the gradient of the time/concentration curve at a given time against $(x/m)_\infty - (x/m)_t$, where $(x/m)_\infty$ is solute loading per unit weight of adsorbent at equilibrium and $(x/m)_t$ is loading per unit weight of adsorbent at time t. This quantity is the unused capacity for constant volume batch operation and is, in conjunction with solution concentration, responsible for the driving force controlling adsorption rate. The advantage of this form is that rate data may be taken directly from the diagram.

A simple linear relationship between rate of adsorption and weight of carbon was expected in the batch experiments. This would be proved by plotting $(x/m)_\infty - (x/m)_t$ against dx/dt for different weights to give

Fig. II:4 Relation Between Weight of Carbon and Adsorption Rate



coincident lines. That this coincidence is not present is shown in Fig. II:4 where the data for adsorption runs in which concentration and volume of dye solution and particle size were held constant, and the weight of carbon added was varied. The tailing off of the straight lines is due to a poor fit of the relationship as equilibrium is approached (Swearingen and Dickenson (1932) originally limited the equation to 80% removal of solute for this reason). It may be due to some comminution of the carbon at the stirring speeds used. For a given unused capacity the adsorption rate is higher for the larger weight of adsorbent. This effect cannot be attributed solely to one cause. It is probable that where a low initial dye/weight carbon ratio was present the concentration of dye in solution was reduced to such an extent by adsorption that equilibrium was achieved by exhaustion of the dye supply, rather than by the carbon capacity being reached. This effect would not be dominant in the runs having higher weight dye/weight carbon ratios. The experimental design was therefore ambiguous in that both initial weight dye/weight carbon ratio and carbon weight were varied. The desired information would have been obtained if the volume of solution was varied to maintain the weight dye/weight carbon ratio constant.

A similar problem is present in the method used to determine the significance of initial dye concentration (Fig. II:5). Dye volume (or carbon weight) should also have been varied in this experiment. Constant volume design alone could explain why the concentration appears to exert a significant inverse effect on rate. Thus it is impossible to recognise if a significant concentration effect is present. A similar erroneous design was used by Weber and Morris (1963a) in an experiment on the effect of concentration on the rate of adsorption of alkylbenzene sulphonates;

Fig. II:5 Relation Between Initial Solution Concentration and Adsorption Rate

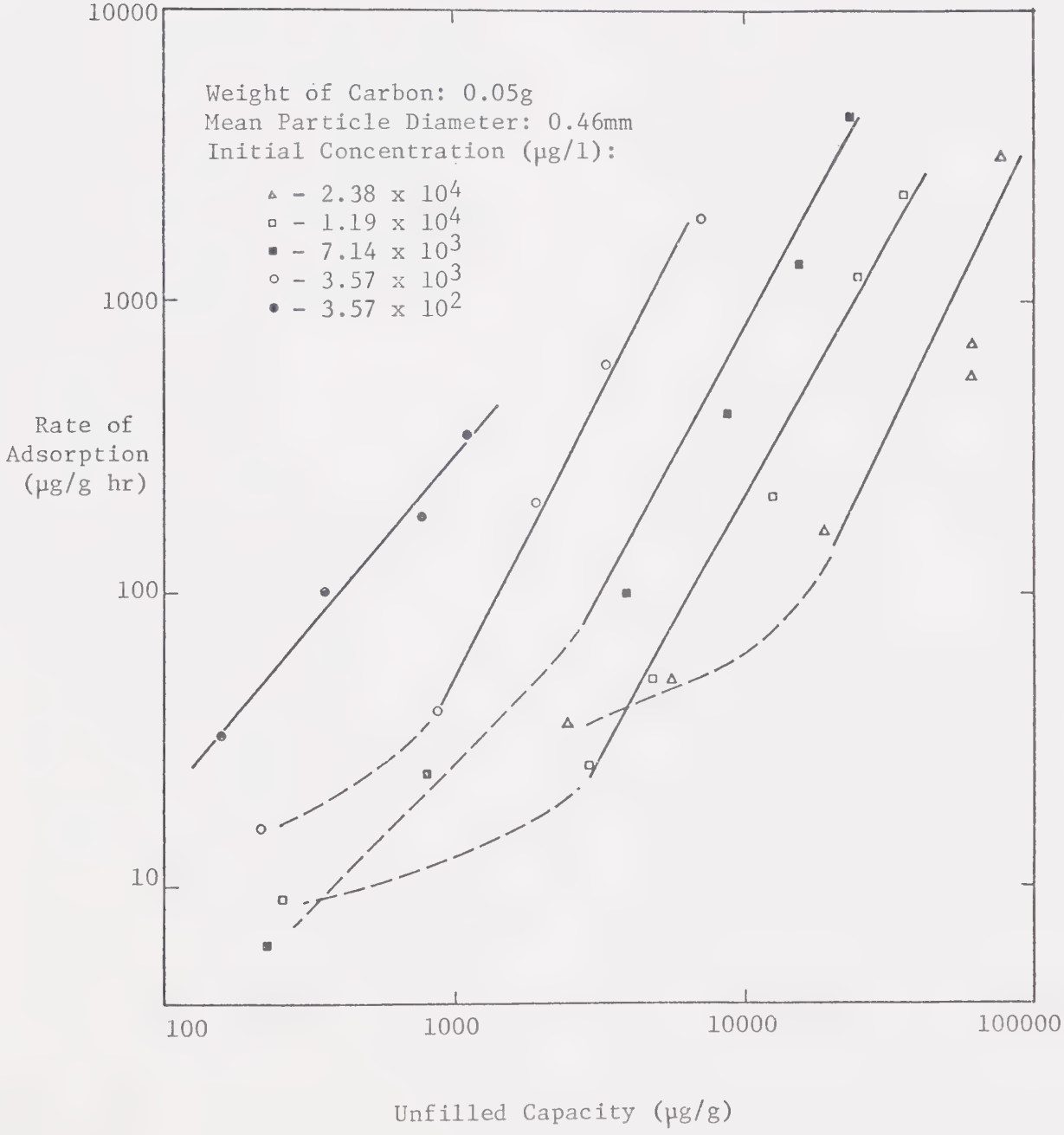
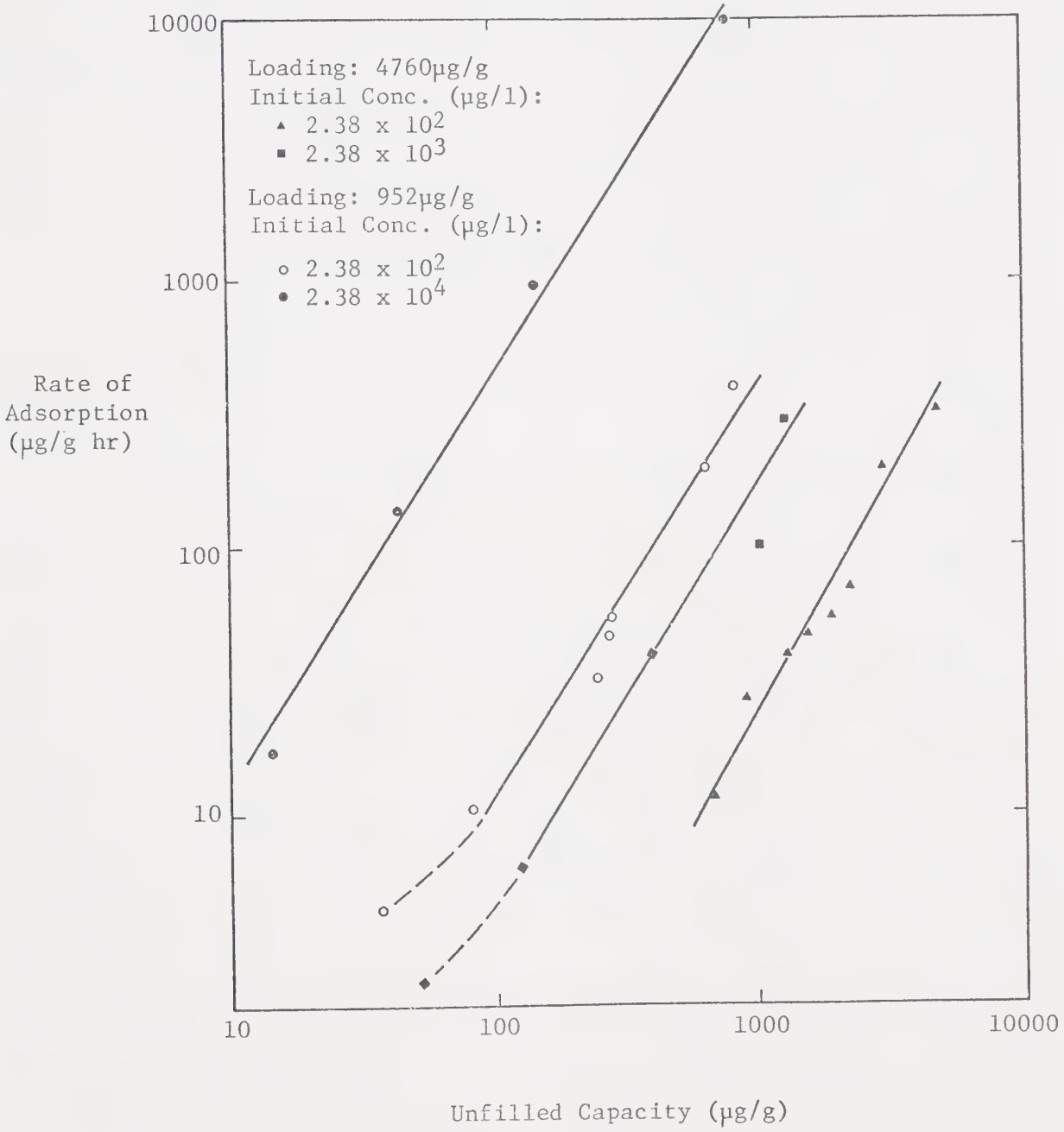


Fig. II:6 Effect of Initial Carbon Weight/Dye Weight Ratio and Initial Concentration on Rate of Adsorption



they were able to show a positive relationship of rate with solution concentration as the range of values used was far lower than in this study.

Data for two sets of runs in which the initial carbon weight/dye weight ratio was constant were obtained. The results (Fig. II:6) indicate that a significant effect is present for both concentration and the carbon weight/dye weight ratio. For a difference in initial concentration of 2.38×10^2 to 2.38×10^3 µg/l adsorption rates are increased approximately seven times, while from 2.38×10^2 to 2.38×10^4 this increase is about thirty seven times. Insufficient points are available to plot this relationship satisfactorily. However it appears that adsorption rates in a field situation will be affected by the normal concentration range experienced.

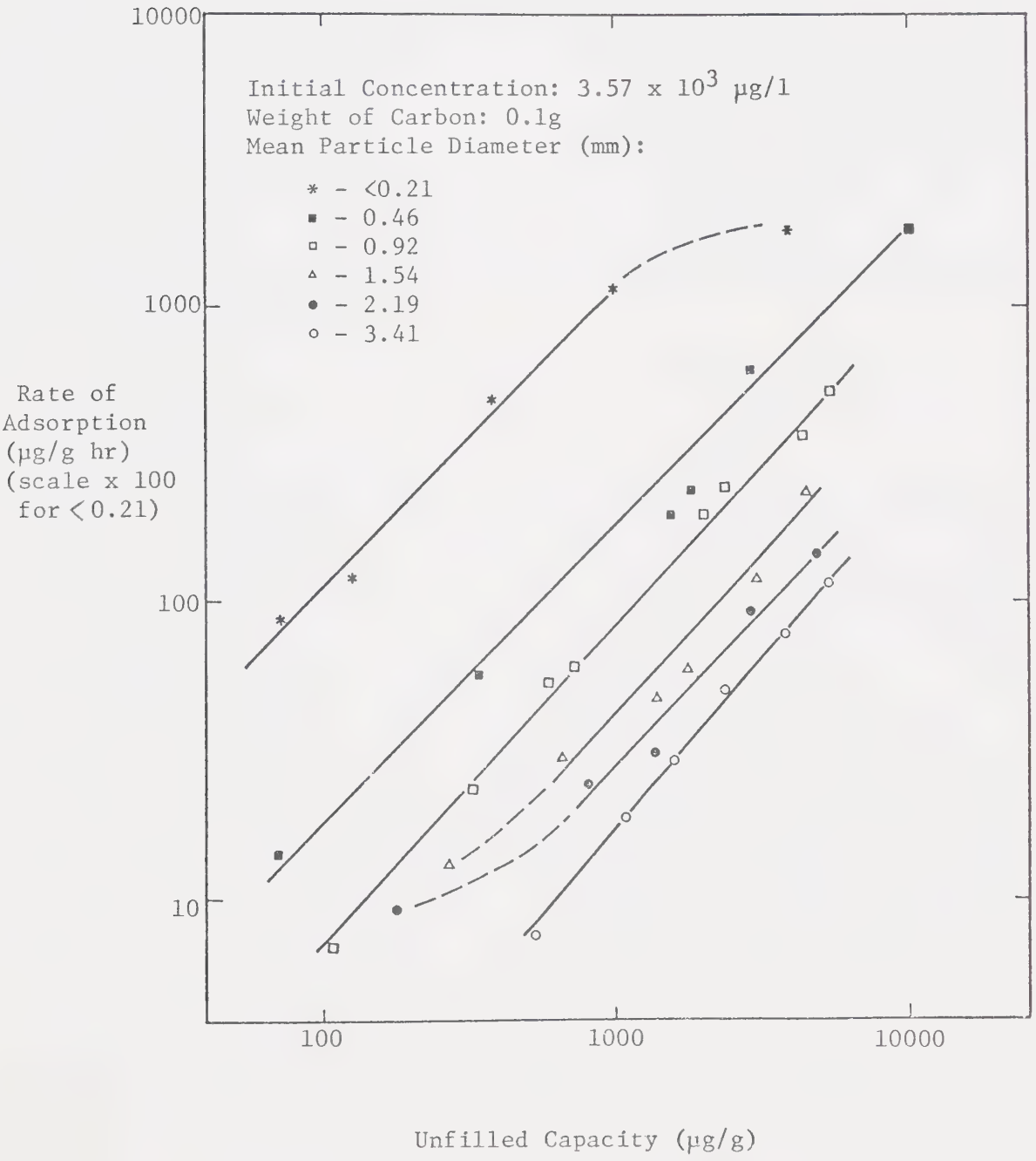
Adsorption may be considered as an equilibrium reaction between a solute phase in the body of the solution and an adsorbed phase on the carbon (Graham 1959, Kipling 1965 p38). Thus both the concentration in solution and concentration on the carbon control the position of the equilibrium. Hence solution concentration would be expected to control rate of adsorption to an equal extent as unfilled capacity - the concentration measurement for the carbon. For a constant mass of dye, changes of carbon weight, like changes in solution volume, affect adsorption rates, via their effect on concentration. It is this indirect effect which has confused the results of the preceeding experiments. Thus from theoretical considerations it is possible to argue that only unfilled capacity and solution concentration control dye adsorption rates; though only the former has been satisfactorily demonstrated in this study. Peterson and Lee (1971) have shown that for a constant concentration experiment, rate

of adsorption of rhodamine B on activated carbon was independant of concentration. This result may be due to the marked increase in capacity with concentration in the constant concentration experiments (which influences the value of $(x/m)_{\infty} - (x/m)_t$) compared to the minor increase for the batch system. Weber and Morris (1963a) however, report a positive effect as has been illustrated in this study, as do Smith et al (1959) for dichlorophenol on activated carbon.

It was hoped to use the concentration/rate diagrams to predict adsorption rates for detectors in the stream. In moderate velocity situations (of the order 0.01 to 0.5m/sec) film diffusion ceases to be rate limiting (Weber and Keinath 1967) and intra-particle transport becomes dominant. This is also the situation in rapidly agitated batch systems, (Weber and Morris 1963a, Smith et al 1959). Hence rate data from these may be transferred to the case of the detector. The detector can be considered a column of very limited length, through which it is assumed plug flow occurs. Given the flow rate through the detector, residence time may be calculated for an incremental thickness of the carbon bed, and hence, given concentration and unused carbon capacity, the amount of dye adsorbed may be calculated. The decreased concentration is then input to the next incremental bed thickness and unused capacity of the first incremental thickness is decreased according to the amount adsorbed. This treatment was first proposed by Peterson and Lee (1971) for industrial adsorption columns. Using the model it would be possible to recommend specific carbon weights for detectors to optimise loading. However the necessary data has not been obtained to predict rates of adsorption at normal field dye concentrations (below about 20µg/l).

The effect of particle size on adsorption rate was studied using

Fig. II:7 Effect of Particle Size on Rate of Adsorption



constant dye concentration, dye volume and carbon weight, but varying the particle size. The data presented in Fig. II:7 is similar to that obtained for other carbon weights and dye concentrations. There is a marked increase in adsorption rate for a given unused capacity with decreasing particle diameter. This rate of increase is higher for the smaller sizes than for the larger indicating a non-linear relationship compared to the linear one observed by Smith et al (1959). It also did not fit the expression of Weber and Morris (1963a) in which rate is proportioned to the inverse of particle diameter squared. Such an expression is expected where intra-particle transport (diffusion) is rate limiting, as is the case in these experiments.

The results were expected in that by decreasing particle size, the average path length for a solute molecule travelling to an internal adsorption site is reduced (Weber and Rumer 1965). This consequently reduces the time required for internal transport as adsorption sites have a higher accessibility. Furthermore the opening up of some previously closed pores may produce a greater connectivity in the grain . It is notable that the finest carbon, which was obtained primarily by hand grinding in a pestal and mortar compared to sieving for the larger grain sizes, had an enormously increased adsorption rate. This may be directly due to the grinding, or more likely is related to the higher capacity of this carbon for dye adsorption. The equilibrium capacity employed was limited by dye availability in solution, rather than saturation of the available adsorption sites, as occurred for the larger particle sizes, where higher equilibrium concentrations (and hence lower loadings) were obtained. Thus once again problems were found with simple constant volume batch experiments due to differences in equilibrium loading of dye on the

carbon.

It is apparent that high adsorption rates are desirable in the detectors to ensure removal of as much dye as possible as stream water passes through them. This can best be achieved by the use of smaller particle sizes,though, as noted before, if the diameter is reduced to such an extent that flow is greatly inhibited the overall effect of the small grains may not be advantageous. For this reason the dusty <0.21mm diameter is undesirable, but the 0.46mm grain size would probably prove sufficiently granular to allow a reasonable flow-through, providing it was limited to relatively thin beds, that is, screen detector type rather than nylon mesh bag.

C. Adsorption Mechanism

A large number of adsorption mechanisms are possible for Rhodamine WT on carbon depending on which properties of the dye are dominant - its weak acidity, its ring structure, the large planar molecular configuration, or the various (unknown) functional substituents in the ring system. Although it is possible by simple experiments to eliminate some of these possible mechanisms, only sophisticated techniques such as electron spin resonance, nuclear magnetic resonance and particularly internal reflectance spectroscopy allow definitive information to be obtained (Mattson and Mark 1971 ch.4). Furthermore, it is likely that several mechanisms may operate in conjunction or at separate points on the surface. The problem is therefore too complex to be dealt with exhaustively in this study.

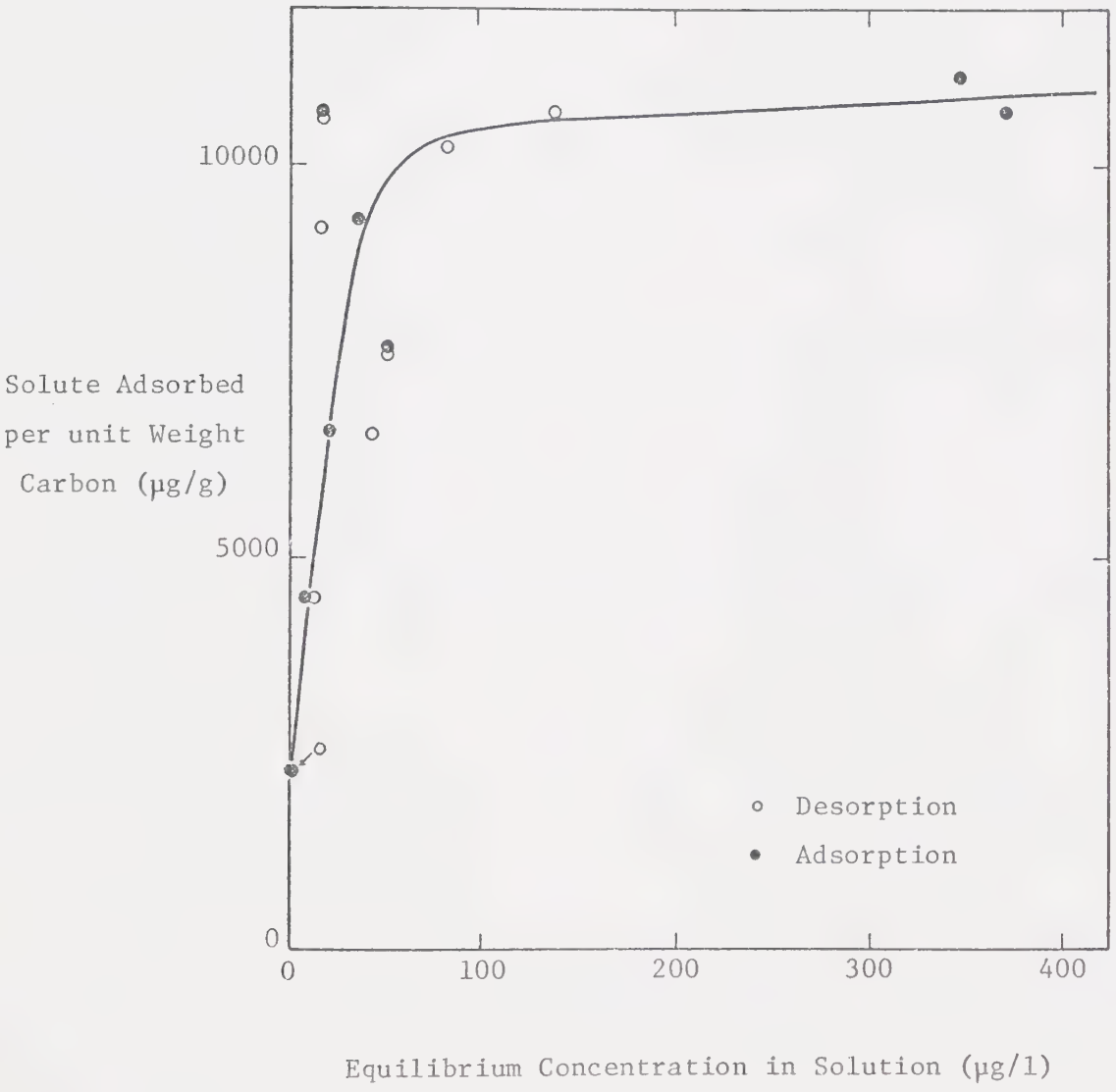
Three basic bond types are recognised to occur: specific, such as a normal covalent bond, which operate between given atoms; non-specific

bonds of coulombic type, which are due to the electrostatic attraction experienced between surfaces of opposite charge; and non-specific bonds of non-coulombic nature, which are due to a variety of inter-molecular forces. Unlike coulombic forces, the latter are effective only over short distances and therefore require close approach of adsorbate to the surface.

In separating between specific and non-specific adsorption, the occurrence of desorption of the adsorbed solute is important. An adsorption isotherm was therefore determined in the normal manner for a carbon of 2.19mm average particle diameter. After equilibrium was obtained, the carbon samples were separated from the solution, washed in distilled water and placed in flasks containing 200ml of distilled water. It was found that desorption occurred until the dye loading and solution concentration were readjusted to equilibrium values (Fig. II:8). However for samples in which all dye had been removed from the solution at equilibrium, desorption did not occur, as would be expected. A constant flow experiment was also used to test reversibility in a more practical situation (see p97 for experimental details and Fig. III:14 for results). This indicated that desorption and/or relocation of dye occurred up to a specific value of loading, after which no more was lost, in accord with the predicted behaviour and the findings of Dunn (1957).

It thus appears that strong specific ion/ion adsorption forces, for instance the Garten and Weiss (1957) carbonium ion mechanism for adsorption of acids, are not operative. This was expected because the negative charge of the dye ion is associated with a large molecule (Kipling 1965 ch.15). However it appears that relatively strong adsorption forces must be operative to prevent complete desorption of the dye as commonly occurs

Fig. II:8 Relation of Adsorption and Desorption Isotherm



in solvent recovery systems. This thus eliminates the variety of ion exchange (Galbraith et al 1959, Giles et al 1964) and hydrolytic mechanisms (Smišek and Černý 1970 ch.4, Hassler 1963 ch.9), which are often completely reversible. Many of these also show a change in solution pH with adsorption (Giles et al 1966). Such a change was not observed in unbuffered adsorption solutions where pH remained constant throughout the adsorption process.

There remain three important adsorption mechanisms: hydrogen bonding between a strongly electro-negative atom and a hydrogen atom, which gives adsorption energies in the upper "physical" range (15kcal/mole) (Graham 1959); electron donor/acceptor complex formation, in which the π electrons of the dye aromatic ring(s) may form either the donor or acceptor (2-15kcal/mole) (Mattson and Mark 1971 p209-222, Coughlin 1969); and van der Waals forces, which cover a variety of inter-molecular forces including Keesom's orientation effect for permanent dipoles, Debye's induction effect and London dispersion forces, which are dominant (2-15kcal/mole) (Smišek and Černý 1970 ch.4). Hydrogen bonding alone, as for other specific bonding, is unlikely to be responsible for all bonding as it is generally non-reversible (Giles et al 1966). However it is quite possible that it is significant for undissociated dye molecules, where a bond may be established between the acid proton, and oxygen held in surface functional groups on the carbon (Ward and Getzen 1970). It may also bond through the amide groups of the dye to surface oxides along the micro-crystalite edges. This may occur for rhodamine B, which is held irreversibly on activated carbon (Peterson and Lee 1971). This is supported by data from the elution studies (Chapter III), which indicate the existence of a polar bond binding a relatively small number of dye molecules.

Such a bond may augment the major bonding mechanism as was proposed for phenol adsorption on activated carbon by Mattson and Mark (1971 p220).

The formation of electron donor/acceptor complexes with the surface by orbital mixing between electron poor and electron rich species produces a dominantly coulombic bond which is generally reversible. The π electron systems of both the aromatic rings in Rhodamine WT and the fused portions of the carbon crystalites are able to enter into such complexes. However as the effect of substituents in such rings is to localise electrons and hence reduce the π electron density, both these groups are liable to be electron deficient, the former because of the various substituent groups on the dye and the latter because of oxygen containing functional groups on the carbon layer edges (Coughlin and Ezra 1968). For phenol and related nitro compounds the complex is formed initially between the phenol π system (acceptor) and carbonyl oxygen groups on the surface (donor), and then for phenol only between the aromatic portions of the carbon surface (acceptor) and phenol π electrons (donor) (Mattson and Mark 1971 p220-21). The former is more likely for Rhodamine WT due to the extent of substitution in the rings, however it must be augmented, perhaps by hydrogen bonding to prevent complete desorption from occurring.

The remaining bonding mechanism is due to van der Waals forces and is non-specific. Due to its rapid distance decay function (force $\propto$ 1/distance^7) it is most effective for flat orientation on basal planes where no surface functional groups are present and where approach of the whole molecular area is possible (Snoeyink and Weber 1967). Bond strength is proportional to molecular size and is also additive, being augmented when the adsorbed molecule experiences forces from both sides of a pore

(Coughlin 1969). Because of the high microporosity of the cocoanut carbon used in this study, it is likely that bonding energies approaching 15kcal/mole may be obtained, comparable to those of hydrogen bonding (Graham 1959). These high energies are indicated by a steep rise in the isotherm and cause retarded desorption (Kipling and Wilson 1960). A flat orientation is adopted at the surface, as for the electron donor/acceptor mechanism, such that multilayer micelles may form, as long as there is sufficient pore volume available (Giles and D'Silva 1969a). The formation of such micelles gives an increase in the overall bonding forces to the surface.

It thus appears that van der Waals forces or electron donor/acceptor complex formation are responsible for the bulk of dye adsorption. No specific information is available to separate these two, but van der Waals forces are most probably dominant, as has been widely suggested for other dyes adsorbed on activated carbon (Steenberg 1944, Giles and D'Silva 1969, Kipling and Wilson 1960, Galbraith et al 1958, Kipling 1965 ch.15, Graham 1955). A variety of bond strengths may be formed such that complete reversibility does not occur, as was suggested by Graham (1959), but hydrogen bonding may also be operative at some specific sites - the active points of Velasco and Ruiz (1948). It is of significance for the practical application of dye adsorption that such active sites will be the first populated on a carbon surface.

3. Environmental Effects

A. Temperature

Batch runs were conducted using 0.1g of carbon of 2.19mm average particle size diameter with 200ml of 3.57×10^3 µg/l dye solution. The

solution was agitated using a magnetic stirrer at a preset speed as the temperature of the enclosure for the large stirrer could not be varied over the desired range. Temperatures of 30°C ± 1°C and 14°C ± 3°C were produced in an insulated inclosure by heating or adding ice as necessary. A constant temperature water bath and oscillating shaker would have been more satisfactory for the experiment but were not available. It was observed that after periods of two or three days fine carbon particles were present in the flasks indicating the stirrer bar caused attrition of the carbon particles.

It was found that the variance of samples at the same temperature was greater than the difference between them. This was probably due to the poor apparatus used in the experiment, but it indicates that a temperature effect of a magnitude comparable to the concentration and loading effects discussed earlier was not present. This finding is supported by Weber and Morris (1964b) who showed that the temperature effect on capacity for alkylbenzene sulphonates on carbon was sufficiently small to be unimportant in practical situations. Lee et al (1965) demonstrated this for eutrophic lake waters by operation of two parallel columns for which a difference in water temperature of 6°C to 23°C gave no significant effect on the amount of chloroform extract of the carbon. Adsorption is exothermic (Weber 1967) and furthermore the magnitude of van der Waals forces decreases with temperature (Kipling 1965 p61), such that a decrease in capacity and mean bond strength with temperature would be expected from theory. This would be augmented by an increase in solubility with temperature (Kipling 1965 p101). A decrease in adsorption of dyes on activated carbon with temperature was reported by Velasco and Ruiz (1948).

Adsorption rate is controlled by a modified diffusion process inside

the carbon grains (Weber and Rumer 1965) and this is temperature dependant with a relationship of the form:-

$$k = Ae^{-E/RT}$$

where k is a rate constant, A is a temperature independant factor, E represents activation energy, T is temperature and R is the universal gas constant (Smith et al 1959, Weber and Morris 1963a). Thus adsorption rate increases with temperature, as has been widely reported, though Weber and Morris (1963a) suggest that the magnitude of the effect is marginal for practical operation.

B. pH

Although pH variations in natural waters are low (pH 6.0 to 9.0), tracing work is often necessary in polluted waters with a much greater pH range, for instance acid mine waste waters. Thus a range of pH values from 13.0 to 4.5 was investigated, the lower end of the range being set by the instability of the dye in acid conditions.

Before the adsorption experiments were commenced the effect of pH on dye fluorescence was determined. A minimum of various acids and alkalis were added to 100ml of 1.19×10^3 µg/l dye solution in 250ml Pyrex-glass conical flasks to produce the desired pH. The flask was stoppered and placed in a light-proof enclosure. Fluorescence was determined through time until no further decrease in values was noted. The time for equilibrium to be obtained varied from 0 to 180hrs in cases where the change was most marked. The systems employed were concentrated hydrochloric acid (35%), concentrated nitric acid (76%) and concentrated sulphuric acid (99%) with solid sodium hydroxide over the complete range, and the

Fig. II:9 Effect of pH on Fluorescence using Different Acids

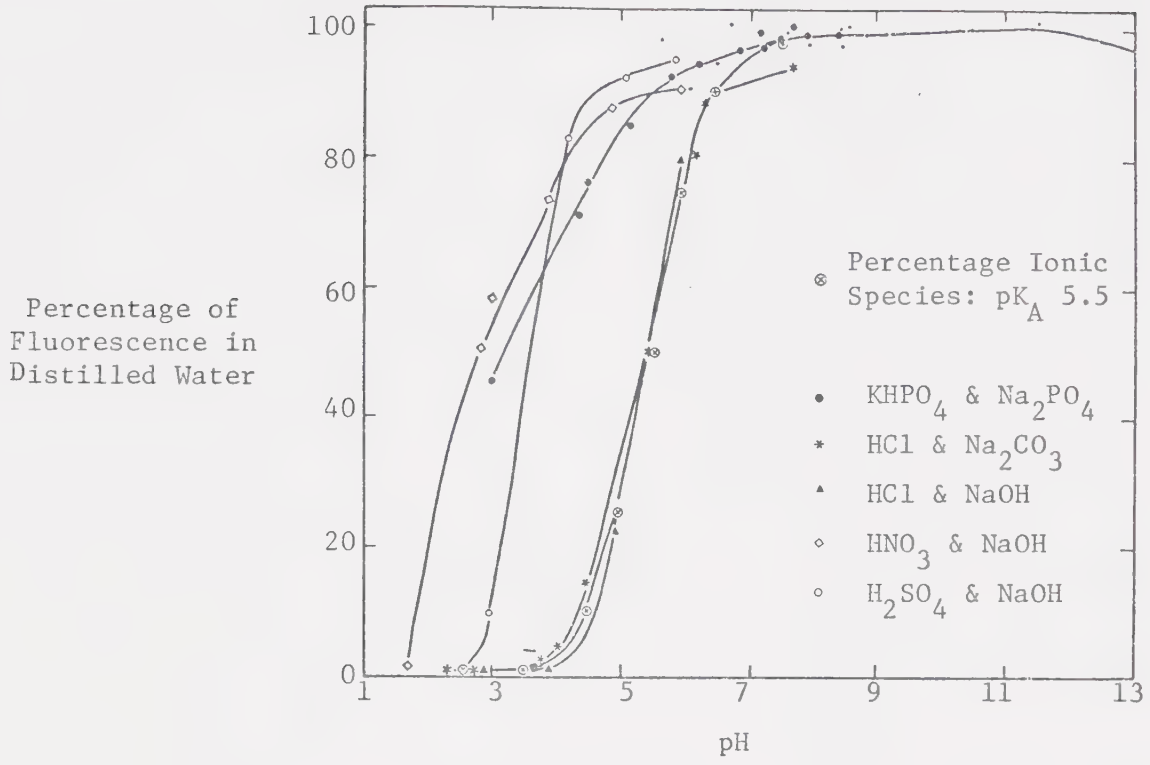
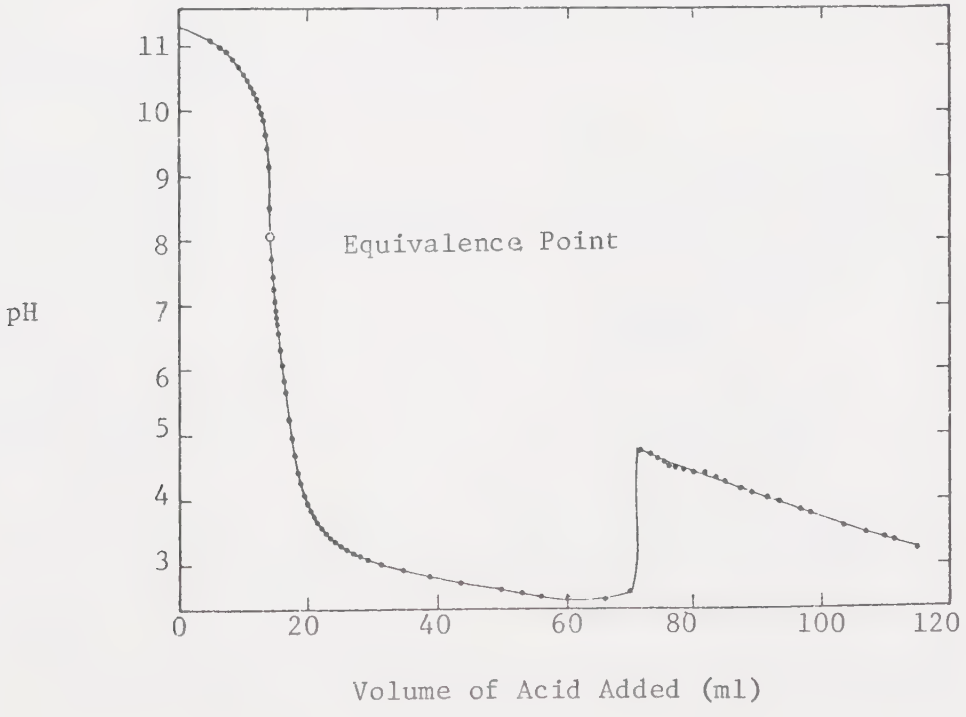
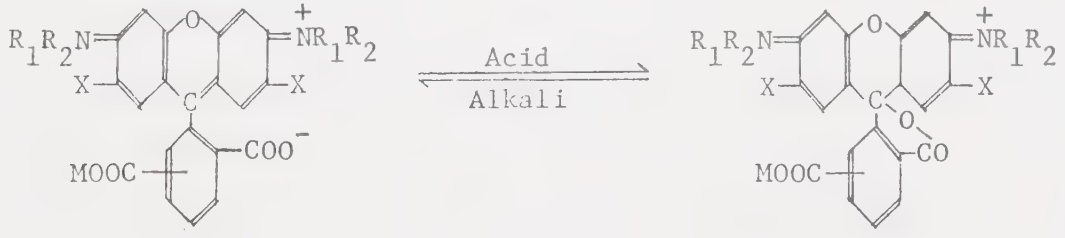


Fig. II:10 Titration Curve for Rhodamine WT with 0.0124M Hydrochloric Acid



phosphate buffer system of Sørensen (Clark 1925 p116) over the range pH 4.5 to 8.5. In the latter system ionic strengths were maintained within the range 0.04 to 0.05. The results are shown in Fig. II:9.

The dye is essentially stable from about pH 8.5 upward, but below this value fluorescence decreases with pH at a rate depending on the acid added. The decrease may be either due to formation of the free acid as the acidic functional groups become protonated with increasing pH, or due to formation of the leuco compound corresponding to the dye. It is possible that protonation will reduce fluorescence by alteration of electron energy levels e.g. Crystal Violet, Pratt (1947 p15-16), Udenfriend (1962 p24-27); some support is given to this argument by the good fit with the percentage ionic species curve plotted for a pK_A of 5.5 (see below p44). However if such a reaction were operative the change would be instantaneous. It therefore appears likely that the colourless lactone form of the dye is produced in an analagous manner to that which occurs in fluorescein and the indicator dye phenolpthalein (Pratt 1947 p189, Conn 1961). This may be dependant on the degree of dissociation of the dye (Udenfriend 1962 p26).. Thus:



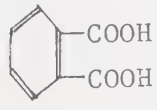
Quinone Form (coloured)

Lactone Form (colourless)

As such a structural change considerably alters energy adsorption wavelengths, a change in fluorescence spectra or complete cessation of fluorescence would be expected. These arguments are only speculative

considering the unknown structure of the dye molecule.

An attempt was made to determine the pK_A of the dye using a standard potentiometric technique, back-titrating with dilute sodium hydroxide from a solution acidified with dilute hydrochloric acid and vice versa. The value of the molecular weight of the dye was estimated, hence the determined value is only an approximation. It was found to lie between 5.1 and 6.0, the lower values being obtained for a solution from which the genenions had been partially removed. Furthermore, the curve (Fig. II:10) showed a peculiar increase in pH near pH 2.5 which was observed also in a replicate run. This may possibly be due to loss of sodium or other alkali ions from a functional group on the dye. Such a suggestion would fit, if the substituted acid groups were in ortho position to each other as the pK_A values for O-pthalic acid are 2.89 and 5.51.



O-Pthalic Acid

Adsorption runs were conducted using standard batch methods employing 0.1g of carbon and 200ml of 2.38×10^3 µg/l dye solution, the pH of which was adjusted using Sørensens sodium phosphate/potassium hydrogen phosphate buffer system with ionic strength ranging from 0.04 to 0.05. A wider pH range was also run using Ringer's sodium phosphate and sodium hydroxide system within the same range of ionic strength (Clark 1925). The phosphate buffer system has been widely used, and was specifically recommended by Andersen (1947) due to its stability in contact with activated carbon.

It was found that the amount of solute adsorbed at equilibrium was

correlated inversely with the carbon weight used, as values of exactly 0.1g could not be obtained. A plot was therefore made of amount adsorbed per g against carbon weight and correction factors taken from a best fit line through the data to adjust loading to an equivalent for 0.1g. This procedure is valid providing that carbon weights were ascribed to different pH values at random, as was the case. The rate constants calculated by plotting log $(C_t - C_\infty)$ against t were also checked for this correlation, but it was not observed to be present.

The data is presented in Fig. II:11. The effect of pH on capacity is barely significant and does not show a marked change near the pK_A value as reported by Andersen (1947) and Ward and Getzen (1970). It is similar, though smaller, to that observed by Weber and Morris (1964b), for alkylbenzene sulphonates, which they attributed to protonation of acidic functional groups on the carbon as pH was lowered. The small magnitude of this effect adds support to the arguments presented earlier that van der Waals forces, not ion/ion interactions, are the most likely adsorption mechanism. It is however important to realise that if loading values on the plateau of the isotherm had been utilised far larger effects would have been measured as demonstrated by Getzen and Ward (1969). This is the case for all the systematic environmental variables tested and means that where very low equilibrium concentrations are being employed, the effect of such variables will be small due to the high bond strength of the adsorption sites utilised.

The effect of pH on adsorption rate is more marked. It is probably due to the same effect mentioned above - the decrease in surface negative charge and dye charge allowing faster diffusion rates and a closer approach to the surface, where the short range adsorption forces can become

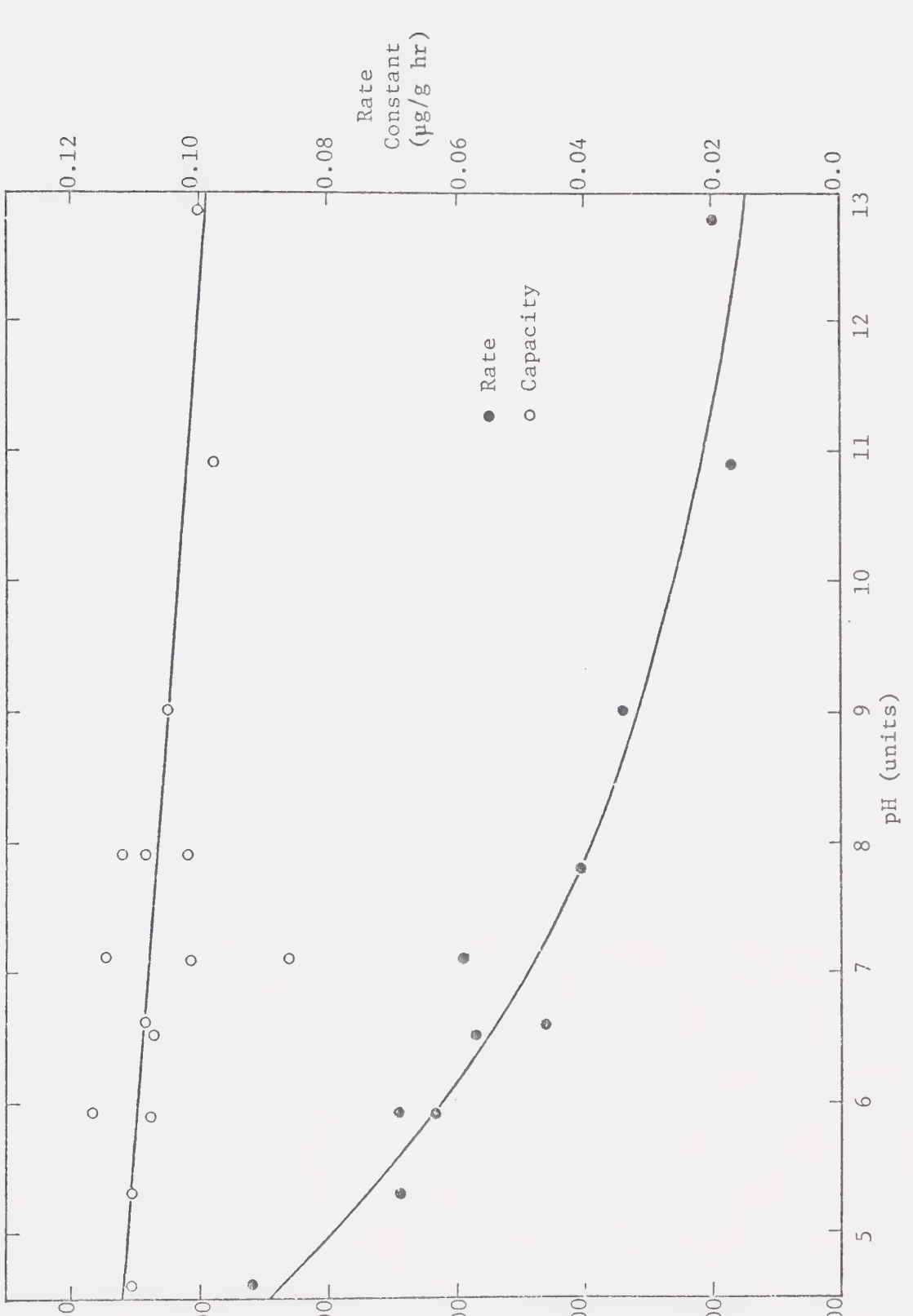


Fig. II:11 Effect of pH on Amount of Dye Adsorbed and Rate of Adsorption

operative (Vickerstaff 1954 ch.4, Weber and Morris 1963a, Cookson 1969).

Thus the pH variation of natural waters will not have a significant effect on carbon capacity or adsorption rate. However larger pH variations will significantly affect the latter. Rhodamine WT should not be used in waters with a pH lower than 6.0.

C. Ionic Strength

The carbon detector technique is normally used in fresh waters with a low ionic strength (max. 0.002), but its use in polluted or marine waters with much higher ionic strengths requires information on the effect of hogh ion concentrations on the adsorption process. The effects of high ionic strengths on the dye were also investigated.

150ml of 1190µg/l dye solution in distilled water was placed in a conical flask and a calculated weight of the solid salt under investigation added. The flask was stoppered and agitated until the salt was dissolved, then the pH was determined using a Sargent Welch Scientific Co. pH meter model PBL calibrated to pH 7, 4 and 10 using standard buffer solutions. The flask was kept in a light-proof enclosure at 21°C, and the pH and fluorescence determined at suitable intervals until no further change in fluorescence occurred. This period varied from 1 to 200 hours depending on the amount of decrease in fluorescence. The neutral salts sodium chloride and potassium chloride were used to compare the effects of different cations, while sodium sulphate, nitrate and bicarbonate (not neutral) were used to compare the effect of different anions. For 1:1 electrolytes ionic strength is equal to the molar concentration of the salt but for 1:2 or 2:1 it is equal to 3x molar concentration (Maron and Prutton 1965 p338-9).

The results are shown in Fig. II:12. It can be seen that the effect

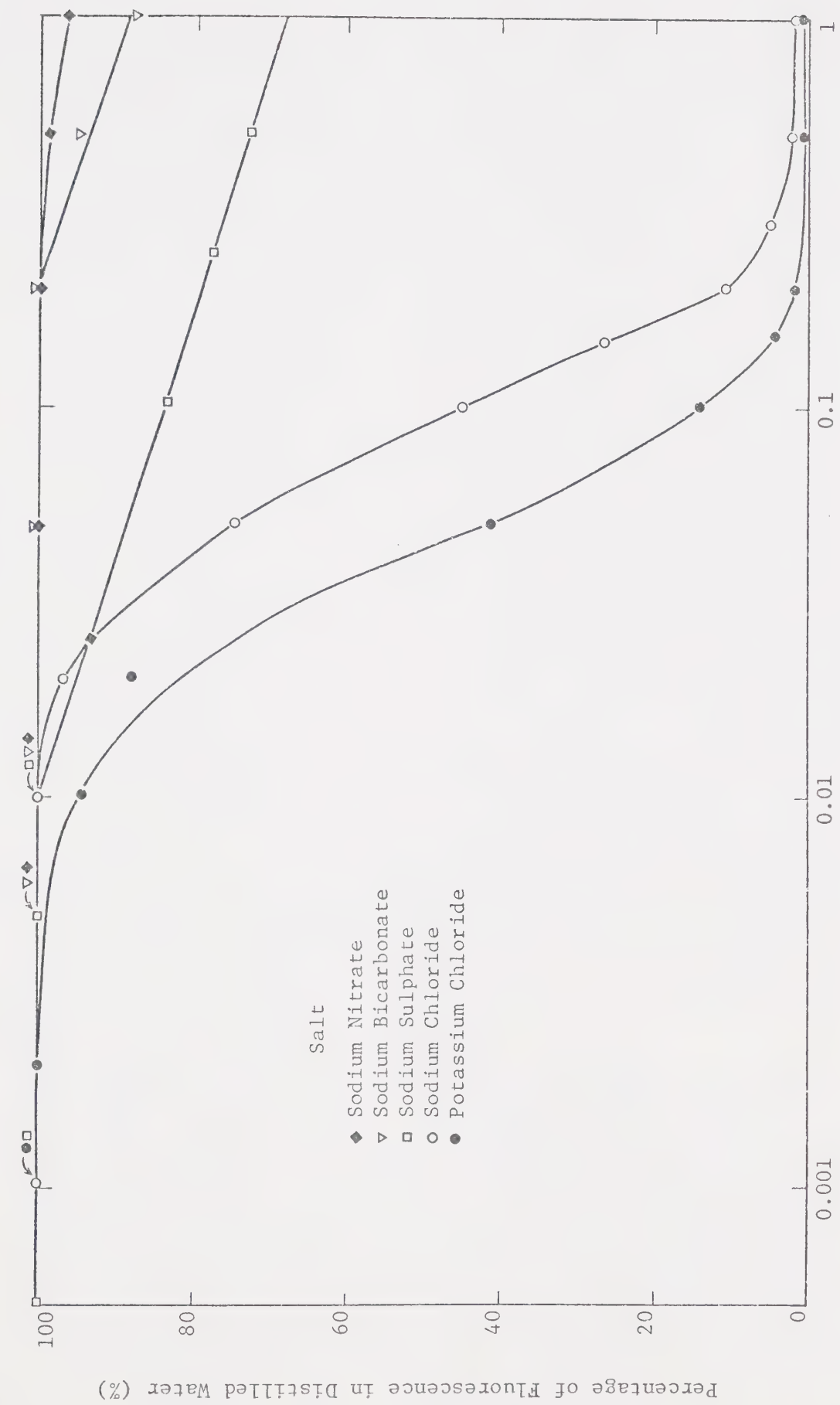


Fig. II:12 Effect of Added Salts on Dye Fluorescence

of the Cl^- ion is far greater than that for $SO_4^=$, NO_3^- or HCO_3^-. There is also a variation in the effect for a given anion with the cation present, perhaps due to common ion effects with the gegenion of the dye. A change in pH toward acid conditions was observed on addition of the neutral salt (from 9.0 for raw dye solution to a minimum of 6.0 for high ionic strength solutions). This was insufficient to explain the magnitude of fluorescence decrease which occurred. However it infers that there was a specific reaction between the dye and neutral salt. Such a specific reaction may explain the significant differences between the fluorescence/pH curves obtained using different acids (above p42). It should be noted that the order of dye susceptibility for the anions is the same in both experiments ($Cl^- > SO_4^= > NO_3^-$). Udenfriend (1962 p109) has noted that halide ions in solution may often cause strong fluorescence quenching in solution, while SO_4^-, for example, does not. This appears to be the case in this study. It is also apparent that considerable changes in the dye adsorption spectra may also occur as colour change in the samples was noted; this alone is sufficient to affect fluorescence. Similar results have been reported by Feuerstein and Selleck (1963) for the effect of sodium chloride on fluorescein, though the effect was similar in form to that for $SO_4^=$ in this study.

The adsorption studies were conducted using standard batch techniques with 200ml of 2.38×10^2 µg/l dye solution and 0.1g carbon. The dye solution was buffered to pH 7.0 using the phosphate buffer system. Ionic strength was varied either by changing the volume of buffer added or adding sodium chloride or sodium sulphate. At low buffer concentrations the buffer capacity was small allowing some pH variation to occur.

Fig. II:13 Effect of Ionic Strength on Carbon Capacity

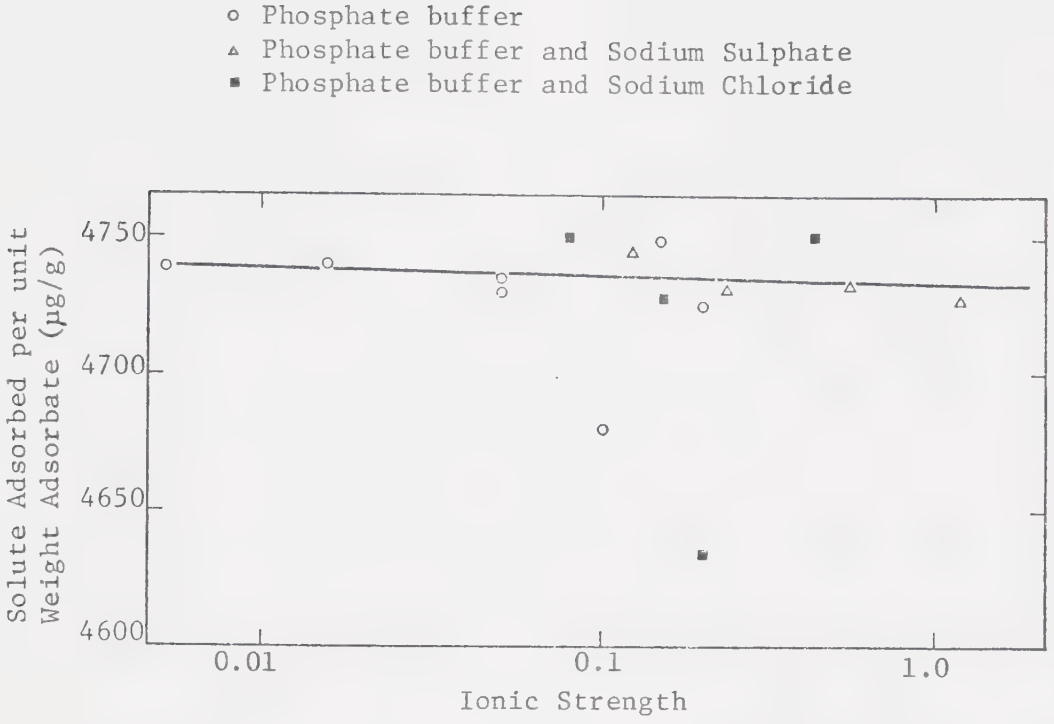
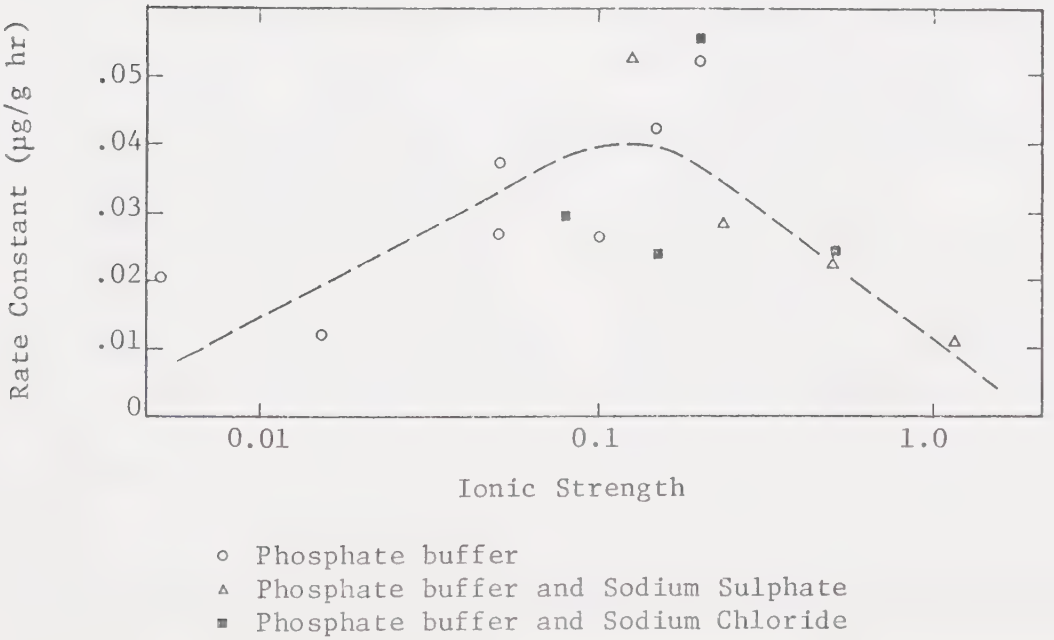


Fig. II:14 Effect of Ionic Strength on Adsorption Rate



Blanks were run, and the concentrations in the samples corrected for decay of fluorescence with time by multiplying by a factor of initial blank concentration divided by blank concentration at that time. This procedure worked satisfactorily for both phosphate buffer and sodium sulphate samples, but produced highly irregular curves for sodium chloride, supporting the suggestion that a more complex process is operative in this case. As the corrections employed were rather small for the other samples the sodium chloride runs were plotted uncorrected. It can be seen that they are of the correct order of magnitude, which was not the case when corrections were applied. A further correction was made to both rate and capacity data for differences in the carbon weight used, as described above (p45).

The effect of increasing ionic strength on carbon capacity is negligible at this loading (Fig. II:13). As for pH, at the low capacity level of operation only high bond-energy sites are utilised, and these are independant of the charge density in solution, once again indicating non-coulombic bonding is dominant. However effects would have been expected from the presence of excess cations, either due to reduction in the energy needed to produce their non-specific adsorption in the surface double layer, or perhaps due to the common-ion effect (Mattson and Mark 1971 p197-8, Vickerstaff 1954 ch.4, Hassler 1963 ch.2).

Fig. II:14 shows the effect of ionic strength on the rate constant k, determined by taking the gradient divided by log e of a $(C_t - C_\infty)$ versus t plot. Two interpretations are possible, firstly that there is an increase in the rate to a maximum about 0.1 to 0.2, followed by a decrease, and secondly that for phosphate buffer, rate increases with concentration, while the reverse occurs for sodium chloride and sulphate.

Further samples would clarify these findings. The results may be explained by reference to two effects: firstly an increase in adsorption rate with increasing ionic strength, due to decrease in the energy needed to bring the dye anion close enough to the surface for physical adsorption forces to operate (the surface is negatively charged at this pH). The second perhaps due to the decay product of the dye being less adsorbable than the unaltered anion, either due to steric effects, or a change in the charge on the anion. More information on the nature of the dye and its decay products is needed before the validity of this explanation can be assessed.

Thus in normal fresh waters both rate and capacity are relatively independant of ionic strength. However in high ionic strength waters the dye stability is relatively poor and appears to affect at least the adsorption rate. When using carbon detectors in such situations these effects should be considered, or another dye used which is not so sensitive to high salt concentrations e.g. Pontacyl Brilliant Pink B (C.I. 45100 Acid Red 52) (Feuerstein and Selleck 1963 p22).

D. Competitive Effects in Adsorption

Several authors have suggested that activated carbon shows a reduced ability to adsorb dye after remaining in a stream for a period of time (Aley 1971) or after exposure to the atmosphere (Drew and Smith 1969). This may be due either to a decay of the adsorption sites on the surface and a hindrance of access to them, or due to competitive effects with other adsorbable materials in the stream. A series of experiments was carried out to evaluate the significance of the decrease in carbon affinity for dye in both air and water.

10g of sorted carbon of average particle size 2.19mm were placed in a 250ml beaker, the top of which was closed by a 15 denier nylon mesh. The output from a constant head tank, which had previously been adjusted to the desired flow, was placed in the beaker and tap water passed through the system. Flow rates of 3.12 l/min, 1.15 l/min and 0.45 l/min were obtained. For the two higher rates the carbon was agitated sufficiently by the water flow, but for the lower one periodic manual agitation was employed to ensure even exposure of the individual grains. Samples were periodically removed from the carbon, washed in distilled water and dried in thin layers in a natural convection oven at 115°C. The drying time varied from 4 to 24 hours, but an experiment showed that variations as large as 4 to 48 hours did not cause any significant effect on the carbon. A batch run was then made using 0.1g of the carbon sample and 200ml of 3.57×10^3 µg/l dye solution according to the normal technique. The equilibrium loading (x/m) and rate constant (k) were determined after completion of the run.

A further 10g of the sorted carbon were placed on an aluminium foil sheet exposed to the laboratory atmosphere, and were sampled and run as above except that oven drying was not necessary.

The results are shown in Fig. II:15 and Fig. II:16. Exposure to a relatively dry atmosphere (average relative humidity of the laboratory over the experimental period was 33% at 21°C) over a 1000hr period produced no appreciable change in carbon capacity or rate constant; the latter showed a rather unsatisfactory degree of variation. Two other carbon samples, air exposed for three and four months, showed no change in capacity or rate from the unexposed carbons. The main aging effect in activated carbon is an increase in the number of acidic oxide

Fig. II:15 Effect of Flow Rate and Time-on-Stream on Adsorption Capacity

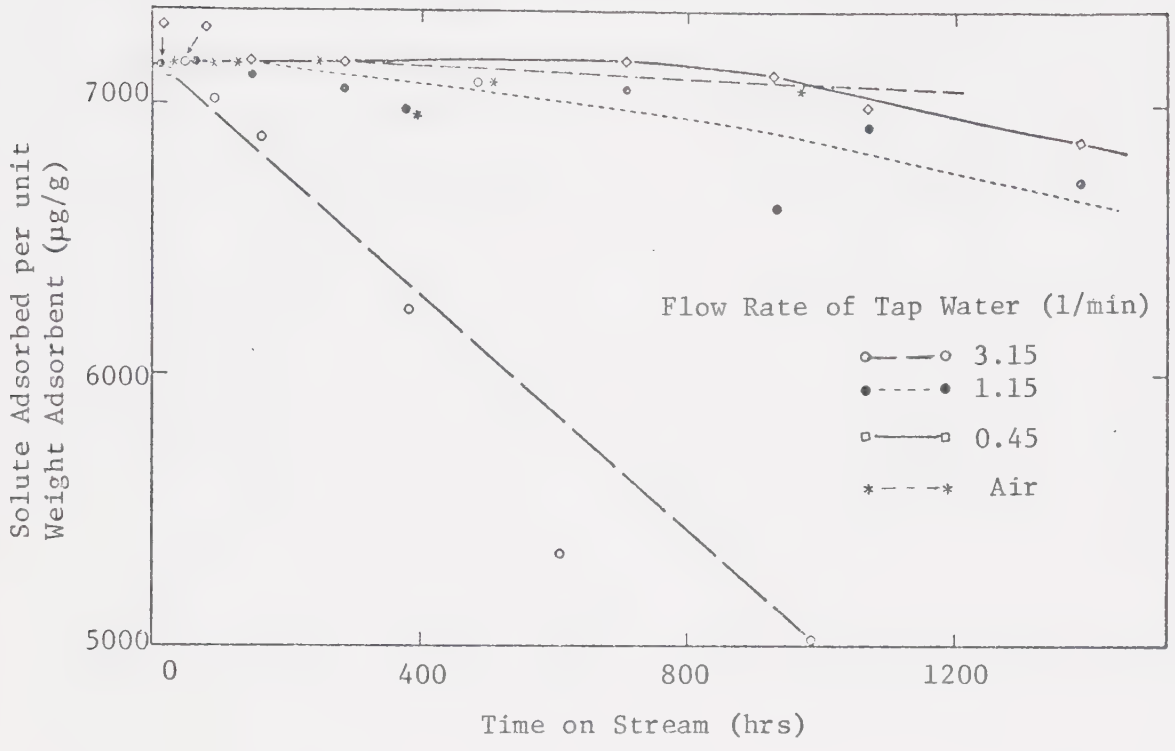
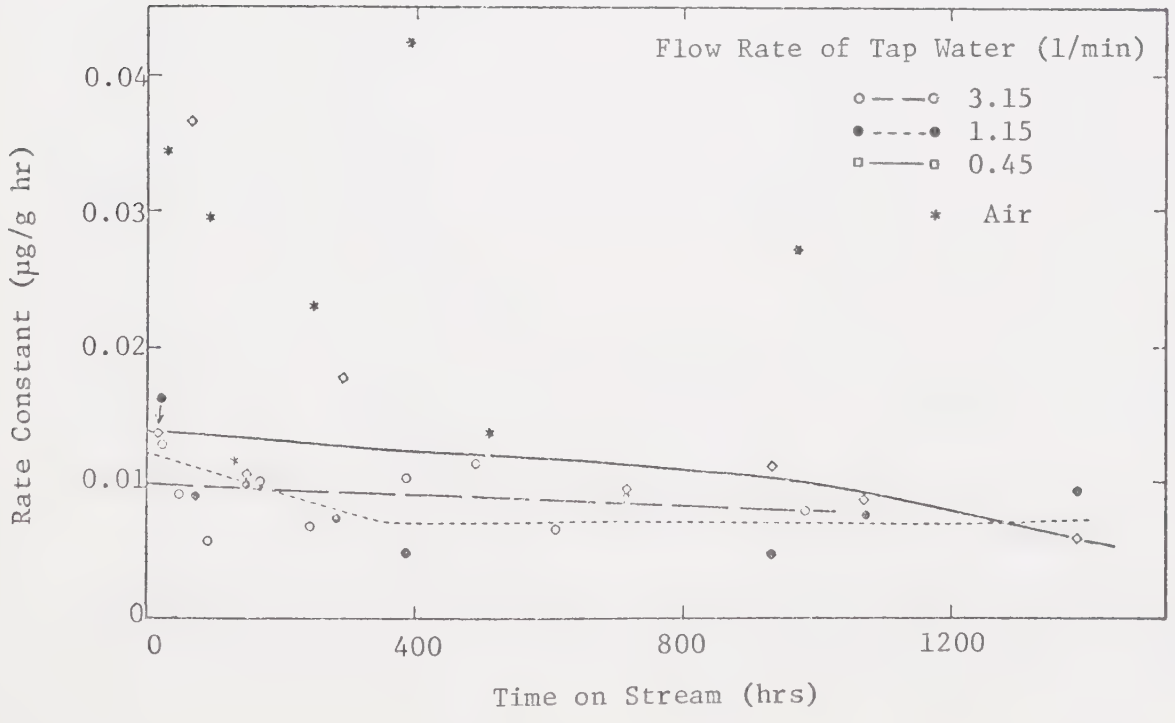


Fig. II:16 Effect of Flow Rate and Time-on-Stream on Rate Constant



functional groups at the surface on exposure to a moist atmosphere (Smišek and Černý 1970 ch.4, Mattson and Mark 1971 ch.2). This would not be expected to affect capacity when van der Waals forces are dominant, but may do so at low pH when hydrogen bonding is possible. It would however be expected to have an effect on the rate constant, the dissociated acidic oxides retarding adsorption and internal transport of the dye anion.

It can be seen that for the flow experiments using tap water, there is a marked decrease in capacity with time, the amount of which is proportional to the flow through the system. The rate data covers a low range and the values show a relatively high variance; however, there is a trend to lower adsorption rate with increased time on stream. It appears that when changes in capacity occur the rate remains relatively constant as is well demonstrated by the two higher flow systems, but not by the low flow one

The decrease in capacity with time is suggested to be due to adsorption of organic molecules from the tap water. These occupy the sites at which the dye would normally be adsorbed, hence reducing capacity. Similarly the adsorption rate will also be depressed due to the lower bonding energy available and the presence of other molecules in the pores. The latter explains why all runs in tap water show rate constants well below that for the aired samples and for those in distilled water. Weber and Morris (1964a) have demonstrated similar effects between several persistent organic pollutants found in river waters.

Support is given to this argument when the relative amounts of organic material in Edmonton tap water are examined. When snow-melt occurs oil and petroleum products from the streets are carried into the river

and hence into the water supply, in which they are sufficiently concentrated to produce both distinct odour and taste. This was observed at a flow time of 900 hours for the two lower flow carbons (the high flow had finished at this time). It can be seen that a change in gradient of the flow time/capacity curves is evident at this point, indicating that increased organic concentration caused a greater decrease in capacity. Quantitative water quality data has not beem examined to support this finding. A batch run using carbons soaked for 1190 hours in tap and distilled water gave capacities of 6880 and 5754µg/1 and rate constants of 0.0184 and 0.0110µg/g hr. for distilled and tap water respectively providing further support for the explanation suggested.

Scanlan (1968) provides interesting support for these arguments. He observed that the background reading obtained on elution of detectors, which had adsorbed no dye, increased with time. Table II:1 shows data abstracted from Table 10 in his study. The values for different times are from neighbouring sites all in the same river. As background

Table II:1 Relation Between Adsorption Period and Background Fluorescence of Detector

Time (days)	Background Fluorescence (µg/1 Rhodamine WT)
0.7	2.5
1.0	4.4
2.0	4.8
3.0	9.6
4.0	14.4
5.0	14.3
6.0	15.6
7.0	10.2
21.0	54.0

fluorescence is due to dissolved organic material in the water, this data illustrates very well how detector capacity was progressively reduced.

It is satisfactory to use carbon which has been exposed to the air for periods of at least one month and probably longer. In situations where high dissolved organic matter content is present in the water, for instance in waters draining a bog or receiving effluent from a town or pulp mill, the detector capacity will be rapidly reduced depending on the flow rate through it. This is particularly important for low dye concentrations in that the high energy sites used are likely to be occupied first by the competing organics. Thus changing the detector more frequently than the recommended one week (Aley 1971) will be necessary.

III ELUTION

1. Introduction

Since the introduction of the charcoal detector method by Dunn (1957), there has been little systematic work to improve the efficiency of the elution process. This is partially due to a lack of understanding of the desorption mechanism involved, which has caused close adherence to previous workers' recommendations, and an empirical approach to development.

This unsystematic process has been accentuated by the lack of sophisticated instrumentation by workers using the technique - the actual efficiency of the method in terms of yield being irrelevant once a dye concentration above the visible threshold has been produced. Thus, if for a given sample a positive test was achieved without use of potassium hydroxide, it was assumed that this reagent was not necessary in all cases. This tendency has probably caused a large number of positive traces to be wrongly assigned to an inconclusive category. Thus considerable resources in terms of man hours and money have been wasted by failure to employ a method which produces a maximum possible dye concentration in the elutant liquid. However, even with the availability of fluorometers and spectrophotometers this "threshold" approach has continued; for instance both White (1967) and Drew and Smith (1969) use the spectrophotometer merely to separate fluorescein from background fluorescence, making no attempt to determine concentration.

It is difficult to assess the validity of much reported work due to the method of presentation normally employed. This is commonly in the form of specific recommendations on techniques, rather than as discussion

Table III:1 Recommendations for Elution from the Literature

This table is not exhaustive - many caving clubs, N.S.S. Grottos and other organisations have limited distribution articles on this topic.

Author	Dye[1]	Weight of Charcoal (g)	Volume of Elutant (ml)	Additive	Solvent	Temperature of Elutant[2] (°C)	Time of Elution (min)	Detection Method[3]	Charcoal Condition	Other
Dunn (1957)	F	few granules	1	5% KOH	EtOH	-	30	V	-	-
Drew (1968)	F & P	As for Dunn (1957)								
Haas (1959)	F	few granules	to cover	5% KOH	EtOH	-	30+	V	-	Add fresh charcoal grain for comparison
Zotter (1963)	F	?	to cover	none	MeOH, EtOH or 2-Propanol	-	until +ve	V	Dry	-
White (1967)	F	As for Dunn (1957)								S used to separate F from background
Bauer (1967)	F	2	7	15% KOH in H_2O	96% EtOH in 1:1 ratio	-	-	-	-	-
Scanlan (1968)	F	6	60	5% KOH	EtOH	21	60	F	Wet	Prewash in dist. H_2O
	RWT	6	60	5% NH_4OH	EtOH	6	60	F	Wet	
Drew & Smith (1969)	F & P	1-10	to cover	10% KOH	EtOH	hot	30	V & UV	-	S used to separate F & P from background
Aley (1971)	F	12	to cover	5% KOH	70% 2-Propanol with H_2O	-	15 to 1440	V	Wet	Test soon after removal
	RWT & PPB	12	to cover	28% (?) NH_4OH	MeOH	-	60	F	Wet	

1. F = Fluorescein P = Pyranine RWT = Rhodamine WT PPB = Pontacyl Pink B
2. Where no temperature given air temperature should be assumed.
3. V = Visual UV = Visual with ultraviolet excitation F = Fluorometric S = Spectrophotometric

of the results of experiments designed to optimise the elution procedure. To the writers knowledge, Scanlan (1968) is the only worker who has presented such experiments. Unfortunately much of his work must be rejected because the comparisons between systems attempted were not controlled with respect to dye loading on the charcoal.

The majority of the work on elution has been with the more commonly used fluorescein/charcoal system. Only Scanlan (1968) and Aley (1971) have investigated the Rhodamine WT/charcoal system with which this work is concerned. A summary of the techniques recommended by various workers is presented in Table III:1.

It can be seen from this Table that recommendations on the elutant composition, temperature, volume in relation to the weight of charcoal, and condition of the charcoal are variable. These are thus obvious variables for investigation. In addition to these "environmental" effects, different dye charcoal interaction effects were also assessed with a view to development of a quantitative process. Variables considered were dye loading on charcoal (loading), the time ellapsed since adsorption (time since adsorption), and initial dye concentration. These three variables were all found to be significant in preliminary experiments.

Several elution techniques are available; the most commonly used is the batch system in which a known volume of elutant is added to a given weight of charcoal, and the dye concentration released is estimated after a given time. This is the best system for visual determination; it is easy to use, and readily reproducible. However, it does not release an optimum quantity of dye because the concentration in solution and on the charcoal reach an equilibrium. The column system , whereby a known volume of elutant is passed through a column containing the

charcoal, does not have this disadvantage. However, it is more difficult to use and reproduce, and yields a large volume of low concentration elutant. In view of the larger quantity of dye released, and the ease of concentration by evaporation, it is surprising this method has not been applied. By employing a Soxhlet extraction apparatus both elution and concentration can be carried out in one process. This extraction technique, which is readily reproducible, is the best available. The apparatus is however fairly complex and expensive.

In the present work a batch system has been used. Tests using the column technique showed that due to varying viscocities the flow-through times varied for different elutants, introducing a further and unnecessary variable. The use of an equilibrium system, whose end point is readily determinable, was also preferable to one where diffusion from within the charcoal could cause an extremely slow approach to this concentration. Furthermore, as the batch system is the most widely used, experimental findings from this study were more readily translatable into practical recommendations. The large number of experiments anticipated precluded the use of a Soxhlet extraction apparatus.

Preliminary experiments were carried out to determine the general form of elution/time curves and to test the batch methods used. It was found that stirring caused comminution of the charcoal particles, and hence a problem in fluorometric analysis due to fine suspended fragments. Attempts to separate these by centrifuging produced enormous changes in the concentration of the elutant (e.g. an increase of 500% for an uncentrifuged concentration of 58 equivalent fluorescence units (see below for definition)). These were clearly erroneous, and could not be explained by either the removal of the suspended matter, volume change, or the

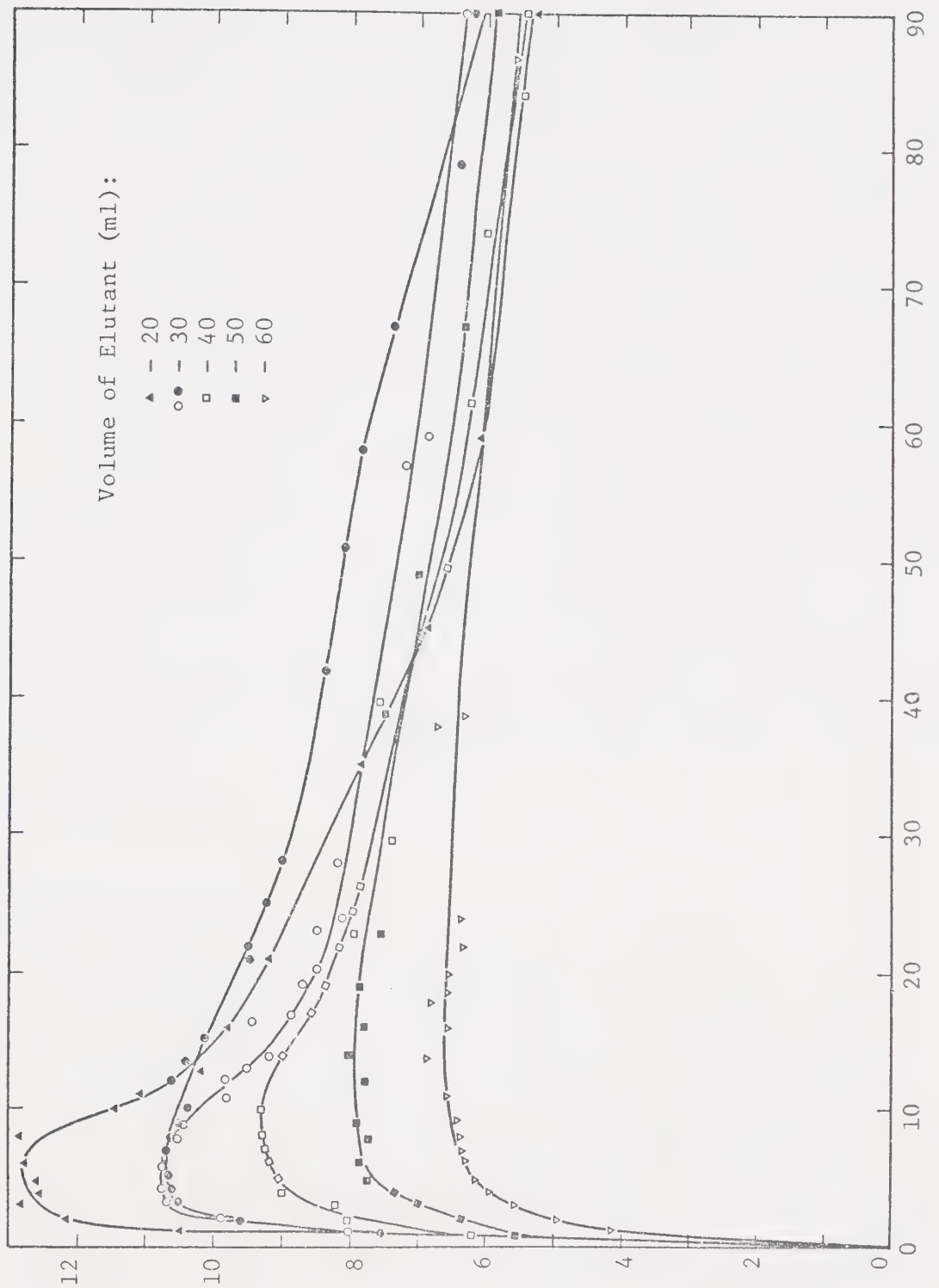


Fig. III:1 Time/Concentration Curves for Elution with 5% Potassium Hydroxide in Methanol

presence of contamination. Their origin remains unsolved. Continuous stirring was not therefore adopted, periodic manual agitation being used.

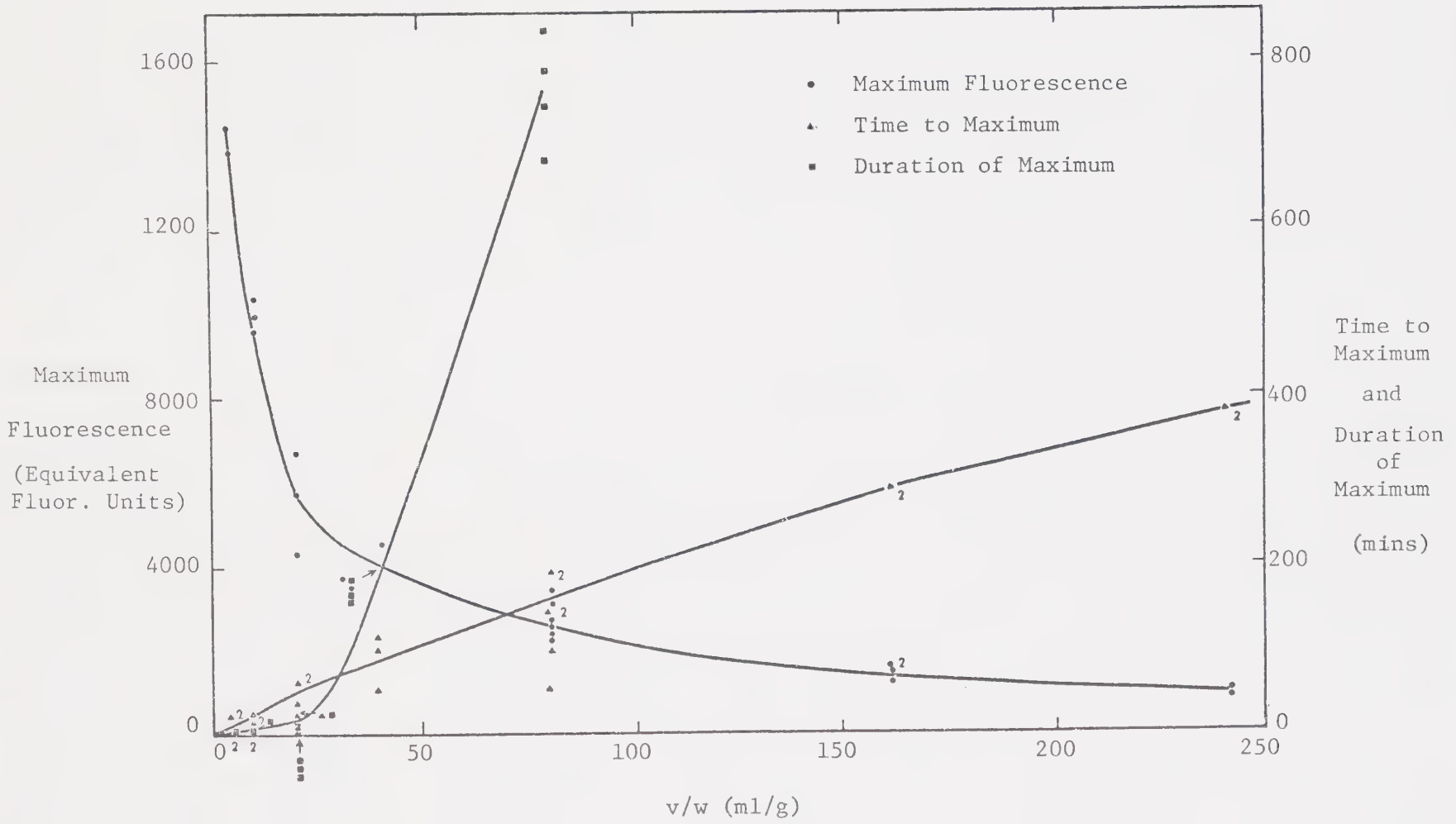
The general form of concentration/time curves for elution is shown in Fig. III:1. Characteristic points on these curves seemed to be initial fluorescence, maximum fluorescence, time to maximum fluorescence and duration of maximum fluorescence. These points were used for comparison purposes in all later work. Fluorescence is employed rather than concentration in view of the large number of calibrations necessary when employing varying elutants. Furthermore detectability is, in many ways, of more importance than concentration. All results were changed to µg/l of Rhodamine WT, using the standard calibration curve for water solvent, and their values expressed as equivalent fluorescence. This effectively linearised fluorescence and produced scale conversion factors. The limitations of this approach are acknowledged.

2. Elution Conditions

A. Weight of Carbon and Volume of Elutant

50g of 8-10 mesh activated carbon were added to a 450ml aqueous solution of Rhodamine WT of 2.38×10^4 µg/l concentration. Adsorption was complete after twenty four hours. The liquid was filtered off, the charcoal washed in distilled water and dried in a natural convection oven in thin layers at 115°C for 24hrs. It was homogenised and samples of the desired weight were transferred into 60 and 125ml ground glass stoppered Pyrex-glass bottles. These were placed in a constant temperature water bath at 40°C to warm. Measured volumes of 75% ethanol in water at 40°C were pipetted into each bottle, and 3ml samples were taken at appropriate intervals for fluorometric determination of the dye released. Sampling

Fig. III:2 Relation Between v/w and Maximum Fluorescence, Time to Maximum and Duration of Maximum



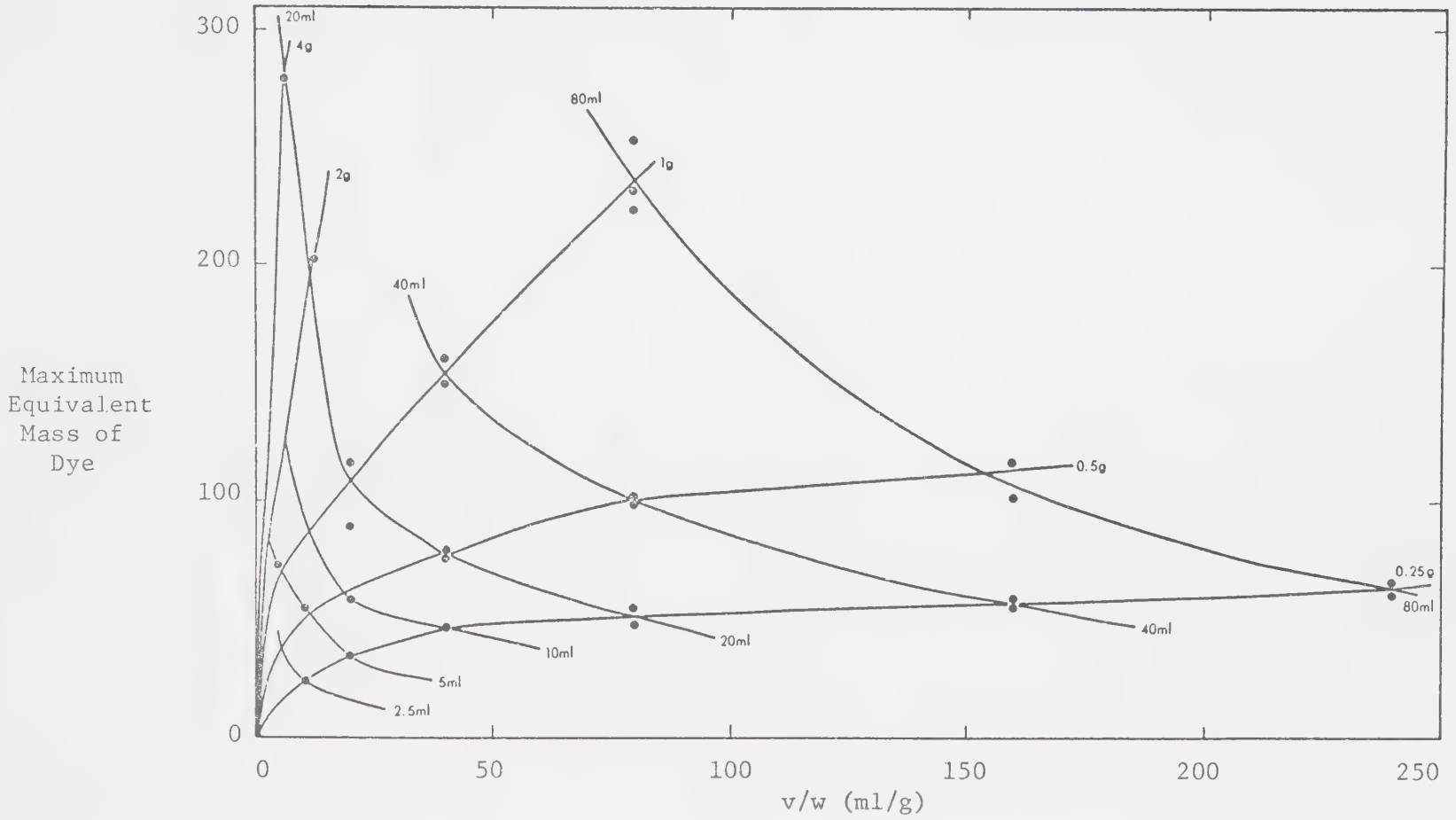
was discontinued when fluorescence had declined from the maximum value. All samples were returned, to avoid appreciable volume loss. Dilution was employed where concentrations were above the range for fluorometric determination. All results were corrected to a temperature of 21°C using correction factors determined during the experiment.

The weights of charcoal employed were 0.25, 0.5 and 1.0g with 80, 40 and 20ml of elutant, duplicate determinations being made. In addition volumes of 5, 10 and 2.5ml were used on the 0.25 and 0.5g weights without replication, and weights of 4 and 2g were run using 20ml of elutant.

Fig. III:2 shows the relation between maximum fluorescence and the ratio of volume of elutant to weight of charcoal (v/w hereafter). There is no difference between maximum fluorescence values for a given v/w produced by varying either charcoal weight or elutant volume. It is evident that low v/w ratios give very much higher fluorescence values than higher ones, readings rising rapidly below a v/w of 10ml/g. The time to maximum increases with higher values of v/w, but the relationship is non-linear. Data for duration of maximum is incomplete due to excessively long times at high v/w values. It can be seen however, that this variable increases very rapidly from zero at low v/w values to times in excess of fourteen hours by a value of 80ml/g.

These observations may be interpreted with reference to two equilibrium reactions occuring in the elution system. The first is between dye on the charcoal surface removeable by elution, and dye in the elutant solution; and the second between the dye in solution and dye readsorbed on the charcoal at vacant sites. The loading used in these experiments is relatively low compared to equilibrium values (429µg/g compared to 1500µg/g) and hence vacant sites, where dye readsorption may occur, are

Fig. III:3 Interrelation of Elutant Volume and Carbon Weight in Terms of Equivalent Dye Mass Released



present. This explains why all elution/time curves studied in this work decrease after reaching some maximum fluorescence value.

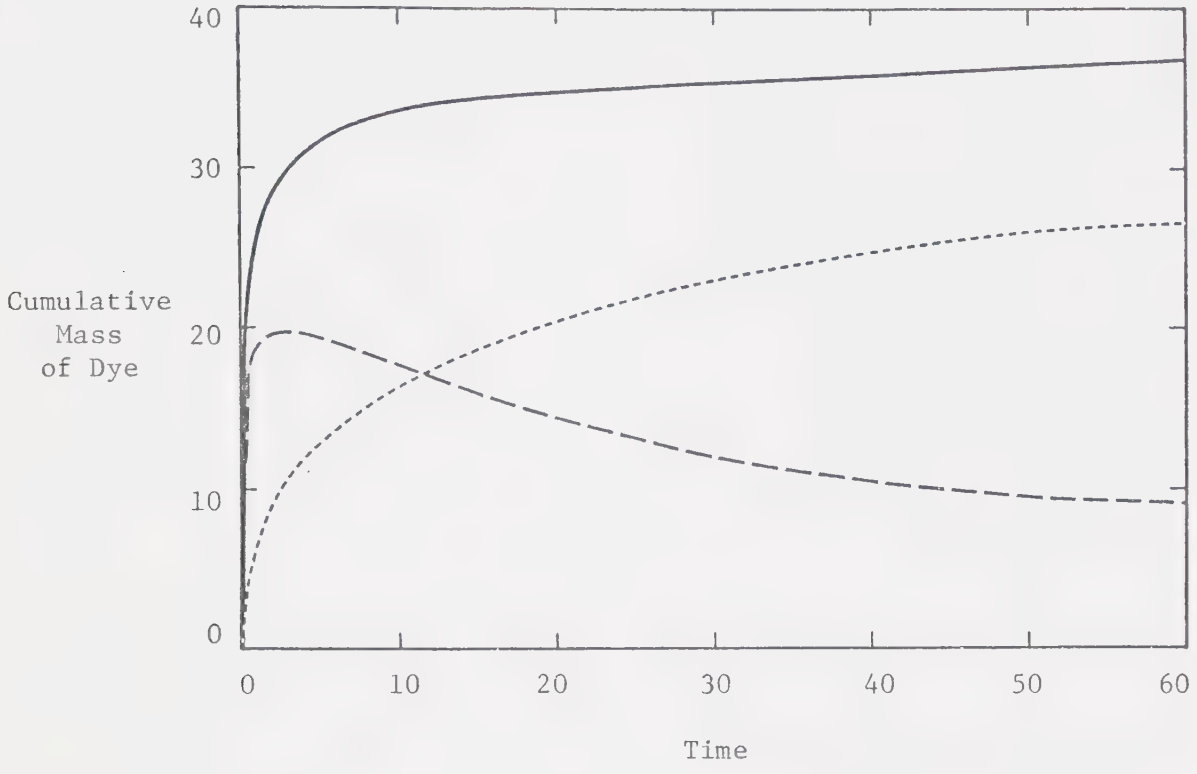
The dominant equilibrium in this system is that between desorbable dye on the surface and dye in solution. This is indicated by coincidence of the values for runs where weight of charcoal alone was varied, with those where volume of elutant only was varied. To produce this result a greater equivalent mass of dye must be removed from the charcoal in high volume solutions than low volume ones of the same v/w value. This is well illustrated in Fig. III:3. Thus relative concentration, not mass of dye released, provides the control on the dye concentration in the elutant.

Examination of the gradients for the equal weight curves in Fig. III:3, shows that for low weights of carbon and high volumes of elutant, little additional dye is released with further volume increase. Higher weights do not show this low gradient. This indicates that dye availability i.e. mass may become a controlling factor with very high volumes, the limit depending on the weight of charcoal (and hence mass of dye) used. This observation is in accord with the differences between batch and column elution, the former with high volumes approaching the latter with low volume.

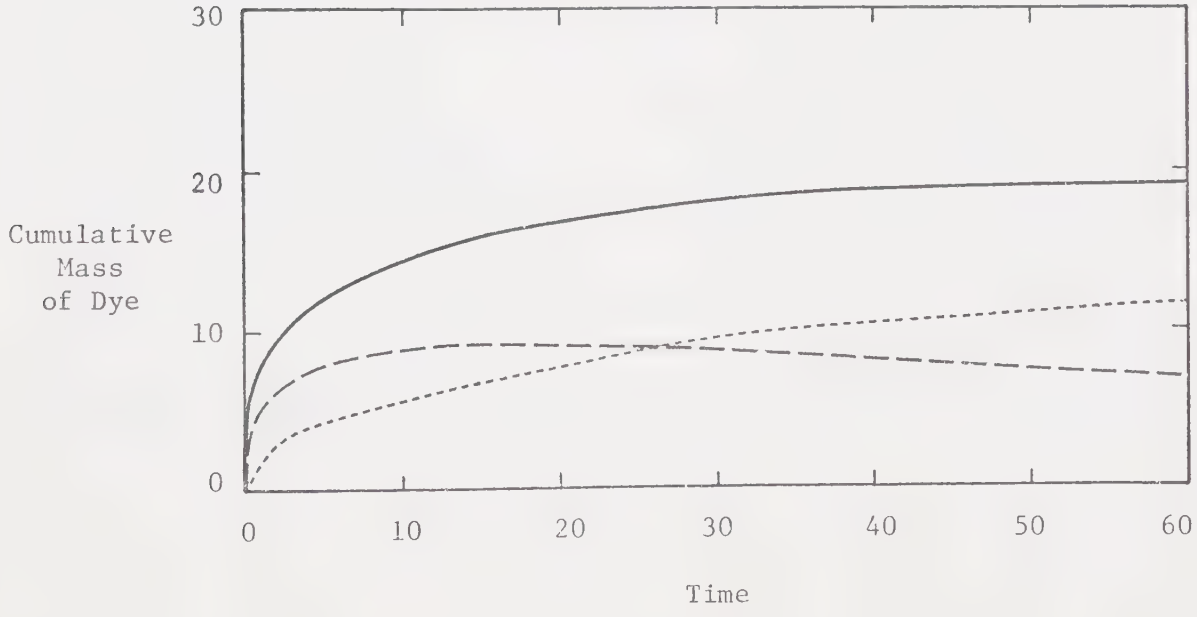
Time to maximum is dominated at low v/w by the initial very rapid release of dye from the carbon surface. This is nearly instantaneous compared to the slower intra-particle transport rate-controlled desorption occuring from inside the particle. It therefore produces very high solution concentrations, which retard desorption of dye from the internal surface of the carbon and also enhances readsorption, the rate of which is proportional to solution concentration (Weber and Morris 1964a).

Fig. III:4 Theoretical Time/Dye Mass Relationships in Elution

A. Low v/w Value



B. High v/w Value



Hence time to maximum is short. (Fig. III:4A).

At high v/w values the concentration of elutant produced by rapid release is considerably lower, permitting effective transport of dye from the internal surface and retarding readsorption. A longer time to maximum results. Due to the far lower concentrations found beyond v/w values of 20ml/g, both desorption and readsorption rates are much lower, the increase of adsorption with concentration being positive and non-linear (Weber and Morris 1964a and above p18). Thus the equilibria will not adjust rapidly, giving low relative rates of change in release and readsorption, and consequently long maximum fluorescence durations (Fig. III:4B). In fact dye release/readsorption into bulk solution probably does not occur at high v/w values, but the dye molecules migrate on the charcoal surface from a release site to a readsorption site.

Thus these results indicate that a column type of operation has an inherently higher minimum detectability, if concentration is employed, due to the increasing weight of dye released with large volumes of elutant. It does however have problems due to extreme equilibrium time. Optimum conditions for batch operation are low v/w, as has been widely employed (Table III:1), and is intuitively correct. If fluorometric detection of elutant concentration is employed, an intermediate v/w is desireable, as this produces an enduring value of maximum fluorescence for determination. It also yields lower fluorescence, allowing easier and more sensitive determination. However, in practise a low v/w value will ensure detection of the eluted dye and is therefore more suitable.

Table III:2 Activated Carbon Samples Prepared for Elution Evaluation Experiment

Code	Weight (g)	Volume of Dye (ml)	Dye Concentration (µg/l)	Time of Adsorption (hr)	Loading (µg/l)
W*	20	500	1.19×10^4	24	298
S	30	1000	4.76×10^3	24	159
M+	25	700	1.19×10^4	48	334
A[x]	20	220	4.93×10^2	24	5.4
N	60	1000	2.38×10^3	480	39.6
T	30	500	5.95×10^3	18	94
V	30	500	1.19×10^4	160	198

* 0.5g samples used.

\+ 40ml elutant used.

x Not standard Carbon.

B. Elutant Composition

Seven lots of activated carbon were prepared with various dye loadings as shown in Table III:2. After adsorption the liquid was separated, the charcoal was washed in distilled water, and dried in thin layers in a natural convection oven for 24hrs at 115°C. The carbon was homogenised and 1g samples were weighed into 60ml Pyrex-glass bottles with ground glass stoppers. The bottles were randomised and numbered.

Twenty one elutants were prepared using methyl and ethyl alcohol as solvents and various concentrations of sulphuric acid, nitric acid, potassium hydroxide, ammonium hydroxide and Fischer "Sparklene" detergent. (see Table III:3). 20ml volumes of each elutant were added to each weighed sample of charcoal, such that a completely crossed two-way experimental layout was obtained. Samples were pipetted from each bottle at appropriate intervals and dye fluorescence determined fluorometrically, until values declined from the maximum. All samples were returned to avoid appreciable volume loss. The experiment was conducted at 21°C $\pm$ 1°C.

The results were analysed in three 2 Way Model I analyses of variance, using the "BIOMED" program BMD02V. Specific contrasts were also calculated using a program written for the Olivetti Programma. It was found that the samples were not completely homogenised with respect to particle size, causing considerable variance in duplicate determinations made from the first and last samples in a batch. Proper randomisation allowed this variance to be estimated in the error or residual variance in the analysis. Also included in this sum were interaction contributions, which were assumed to be negligible. The Analysis of Variance Tables are given in Table III:4, and the marginal means for all elutants, which give

Table III:3 Marginal Means from Elutant Evaluation Analysis of Variance

Elutant (% bt wt.)	Maximum Fluorescence (Equiv. Fluor.Units)	Time to Maximum (mins)	Duration of Maximum (mins)
Methanol			
1% KOH	137	22	28
5% KOH	124	11	14
0.5% H_2SO_4	109	14	18
5% H_2SO_4	65	9	28
0.5% HNO_3	98	30	21
5% HNO_3	46	10	14
1% NH_4OH	424	42	48
5% NH_4OH	288	50	49
10% NH_4OH	149	35	49
100% Methanol	316	26	35
Ethanol			
1% KOH	83	83	25
5% KOH	50	44	16
0.5% H_2SO_4	270	61	47
5% H_2SO_4	193	27	56
0.5% HNO_3	234	90	38
5% HNO_3	148	58	36
1% NH_4OH	287	109	49
5% NH_4OH	681	46	53
10% NH_4OH	648	179	74
Detergent	558	23	98
100% Ethanol	115	14	56

Table III:4 Results of Analysis of Variance for Elutant Composition Experiment

Maximum Fluorescence

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Squares
Elutant	20	5126000	256300
Carbon	6	9700000	1617000
Residual	120	8530000	71080
Total	146	23360000	

Elutant and Carbon effects both significant at 99.9%

Time to Maximum

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Squares
Elutant	20	232500	11630
Carbon	6	82830	13800
Residual	120	294600	2455
Total	146	609900	

Elutant and Carbon effects both significant at 99.9%

Duration of Maximum

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Squares
Elutant	20	61980	3099
Carbon	6	34980	5829
Residual	120	51770	431
Total	146	148700	

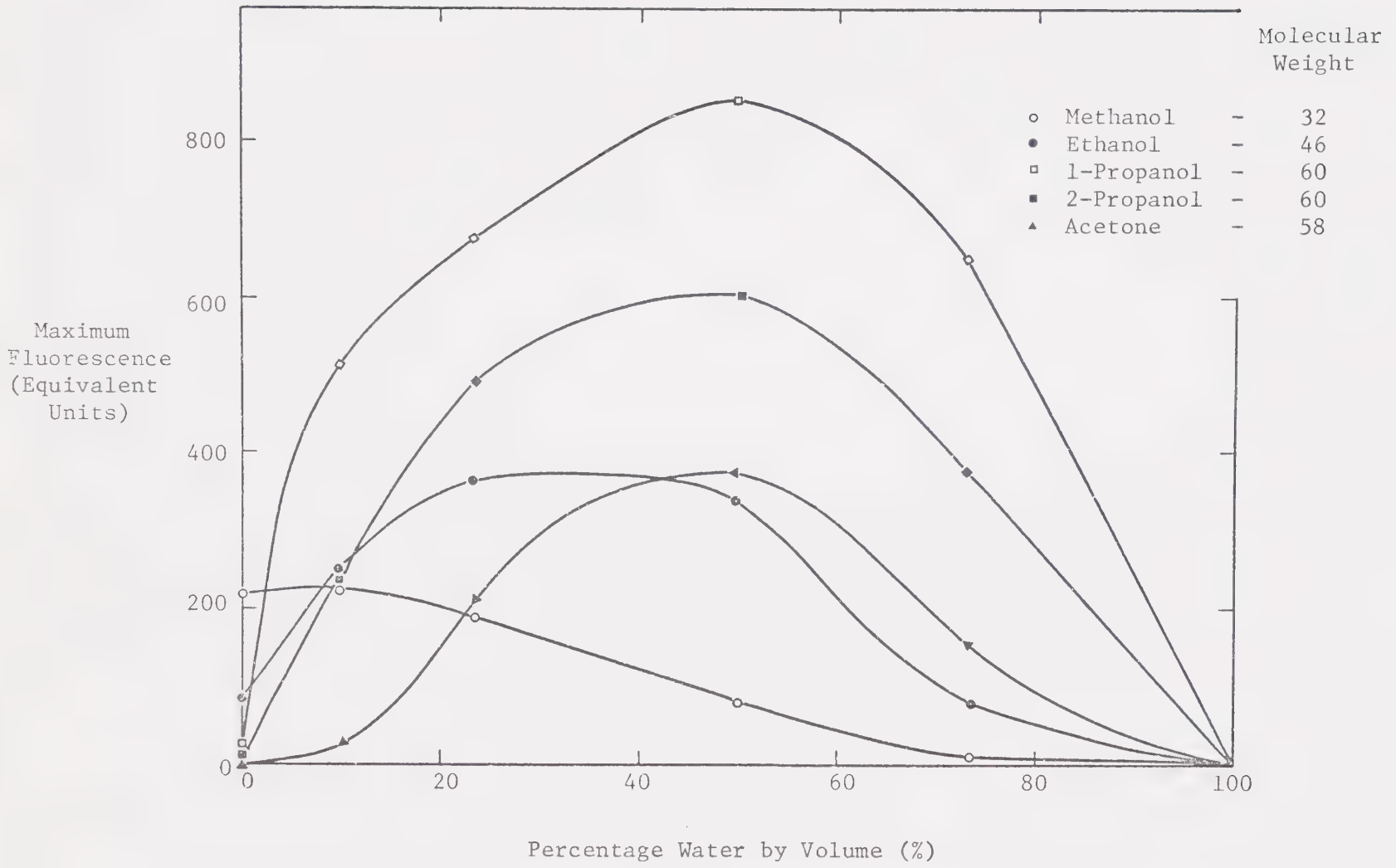
Elutant and Carbon effects both significant at 99.9%

true estimates of effects in the analysis of variance, in Table III:3.

Both elutant and charcoal effects were highly significant, therefore specific contrasts to determine the best elutant, in terms of maximum fluorescence yield, were calculated. Maximum fluorescence gives an estimate of maximum detectability as it comprises both fluorescence efficiency in the solvent and dye concentration. It was found that the use of ethanol as solvent gave significantly higher yields than methanol (at 95% significance level); this result was also found for samples with ammonium hydroxide additive only. The 1% and 5% concentrations for this additive gave significantly different results (99% significance) but the 5 and 10% results were statistically inseparable as was the 5% and 10% compared to detergent. It can be seen that the use of acid additives was not successful; both these and potassium hydroxide giving inverse relationships between concentration and maximum fluorescence, indicating supression of dye release. Other additives which were examined were lithium hydroxide, sodium hydroxide and detergent (in methanol) and other solvents chloroform, benzene, butanol, acetone and turpentine. None of these were successful.

It was noted that an approximate relationship between the water content of elutant and its yield was present - potassium hydroxide prepared from a solid was very poor, the acids, produced from very concentrated solutions (99%, and 76%), were intermediate, while ammonium hydroxide, from a 28% solution and detergent in a 50% solution, were both good. A second experiment was therefore prepared to investigate the influence of water percentage on elution. 1-propanol, 2-propanol and acetone were used in addition to methanol and ethanol, because dye release appeared to increase as the primary alcohol series was ascended.

Fig. III:5 Effect of Water Content on Fluorescence Maximum for Water Miscible Primary Alcohols and Acetone



1g portions of a carbon loaded with 78µg/l of dye (30g carbon plus 500ml 4.76 x 10^3 µg/l solution for 24hrs) were weighed out into 60ml Pyrex-glass bottles with ground glass stoppers. (It was found in the previous experiment that loading did not change the relative order of elutants with respect to maximum fluorescence values). These were randomised and, to each, 20ml of the selected solvent/water mixture was added. All solvents were completely miscible, hence butanol was not included in the experiment. 3ml samples were taken at an appropriate time interval, and their fluorescence determined on a fluorometer, until the values decreased from the maximum. All samples were returned to the bottles to avoid volume loss. The temperature was 21°C $\pm$ 1°C.

The relation of maximum fluorescence to percentage water in the elutant is shown in Fig. III:5. It can be seen that there is a large difference in fluorescence values due to the use of different alcohols (the higher the molecular weight the more dye released). Molecular geometry is also significant, the straight-chained 1-propanol being significantly better than the branched-chain 2-propanol, which is better than the corresponding ketone acetone. Furthermore, ascending the homologous series there is a trend towards higher percentages of water producing maximum fluorescence. On applying calibration correction factors to allow determination of absolute concentrations, the curves are reduced in magnitude but show the same overall form, indicating that the effect is not merely due to the influence of solvent on the quantum efficiency of fluorescence. The results are in contrast to the work of Hassler and McMinn (1945), who showed a simple inverse relationship between the amount of malachite green adsorbed and percentage ethanol in solution. (Amounts adsorbed and desorbed are inversely related).

Moloney and Findlay (1924) suggested two basic mechanisms of desorption, while Hassler (1963 p245) added a third:-

1) Lowering the potential for adsorption of a solute: this includes changing the solvent system and other solution conditions, such as pH and temperature, to cause desorption. For instance methyl violet may be released from charcoal by use of ethanol as a solvent.

2) Replacement of adsorbed phase with another substance: for instance desorption of methylene blue, safranin and methyl violet with aqueous soap solutions.

3) Alteration of the chemical nature of the surface or adsorbed phase to cause release: for instance conversion of organic acids to their sodium salts may cause partial release from charcoal.

Mechanism 3) above appears unlikely because, although there is a change in the dye spectra in ethanolic solutions, the dye appears substantially unchanged. Furthermore the exact nature of such a change under the prescribed conditions is somewhat problematic; at most it could be a disruption of dye micelles due to association with the solvent. The solubility enhancement approach is also unsatisfactory; although temperature and pH do cause differences on elution, these are minor when compared with the effects of changing the solvent. The latter is therefore the controlling factor. As Rhodamine WT is a polar dissociated organic acid, its solubility in water is high. It is unlikely that it becomes increasingly soluble as the alcohol used becomes more hydrocarbon in character. This is supported by its very low solubility in benzene and chloroform. However desorption increases markedly ascending the homologous series and is zero for water alone, thus disproving this mechanism.

Replacement of the dye by adsorption of another molecule, in this

case the solvent, therefore appears likely. This is supported by the data in Fig. III:5. Adsorption of alcohols (equated with desorption of the dye) follows the modified form of Traube's Rule, which states that increasing adsorption is expected ascending a homologous series. (Hassler 1963 ch.9, Kipling 1965 p179-181, Weber 1967, Smišek and Černý 1970 ch.4, Mattson and Mark 1971 p167-170). Furthermore steric effects in branched-chain molecules are well known to cause decreased adsorption (Dzhigit et al 1948, Hassler 1963 ch.9, Weber and Morris 1964b, Smišek and Černý 1970 ch.4), as is found in the case of 2-propanol. It is now necessary to consider the mechanism of this replacement.

The mechanism of dye adsorption was discussed previously; it was concluded that van der Waals forces were probably responsible, though electron donor/acceptor complex formation and a small amount of hydrogen bonding may also be important. These conclusions are supported by the elution studies. If van der Waals forces dominate adsorption, Davies (1968) argues, then the tendency for a system to reach the lowest possible energy state will preclude the replacement of a large molecule by a smaller one, due to the lower free energy of adsorption of the smaller molecule. Evidence to support these arguments have been presented by Giles and D'Silva (1969) for anionic and cationic dyes adsorbed on activated carbon and bone char. One dye may replace another on the surface only if it has a larger molecule, and hence larger van der Waals attraction. In the elution work presented, it is clear that relatively small molecules are responsible for displacement of the much larger dye from the charcoal surface.

The simplest explanation for this effect is that the dye is adsorbed by some specific interaction with a surface functional group or site,

for instance by hydrogen bonding (Ward and Getzen 1970), for which the alcohol has a greater affinity. Both Smišek and Černý (1970 ch.4) and Kipling (1964 p173) note that alcohols are bonded onto polar functional groups, rather than being held by van der Waals forces. The latter author suggests hydrogen bonding between the alcohol and oxygen or other electro-negative atoms in the functional group, is the cause of this strong attraction. Coughlin (1969) presents data for gas adsorption of methanol, which shows that 40% of the bonding energy onto a carbon surface may be attributed to dispersion forces, while 60% is from interaction with permanent dipoles. It therefore seems likely that displacement of dye on polar sites by alcohol can occur. Hassler (1963 p200) provides support for this view by showing that specific sites are occupied both by methylene blue and malachite green on various carbons, which ethanol is capable of blocking.

However, the polar nature of alcohols decreases with an increasing number of carbon atoms, and, as has been shown by Gasser and Kipling (1970), the adsorption on polar sites becomes less. It is therefore difficult to explain the marked reverse effect in the elution experiments if only polar sites are considered. Alcohols are also adsorbed from aqueous solutions where no polar sites are present, for example on Graphon, a high temperature modified carbon black (Hansen and Craig 1954), or when polar sites have been saturated (Gasser and Kipling 1960). In these instances van der Waals forces are operative. Hence the effects of increasingly hydrocarbon character ascending a series, and the resultant increased solute/water repulsion operate (Weber 1967). This is indicated by the increasing heat of adsorption found ascending a homologous series and, less regularly, with increasing molecular weight; furthermore the

value for straight-chain molecules is higher than for the equivalent branched-chain. (Hassler 1963 ch.9). Thus Traube's Rule applies as was shown for primary alcohols in aqueous solutions by Dzhigit et al (1948). This appears to be the case in elution experiments.

Recently Manes and co-workers have developed the Adsorption Potential approach of Polanyi for adsorption from solution. Manes and Hofer (1969) have shown that it gives reasonable prediction of results for two dyes in various solvents. They therefore suggest that where van der Waals forces are operative the extent of desorption for a given solvent may be found from the adsorption potential of the solute in that solvent. The adsorption potential can be calculated from a characteristic adsorption curve, the solubility of the solute in the solvent and the molecular polarizability of solute and solvent. (Hofer and Manes 1969). The theory predicts the most significant effect, for a given solvent, on systems of high molecular weight solutes and low loading. This approach is in contrast to that of Davies (1968) discussed above, in that it allows for elution of large molecules by ones of considerably smaller size.

Thus in the elution experiments, although some of the dye may be released by the bonding of alcohols onto polar groups, it is probable that the larger alcohol molecules operate by competitive adsorption dominated by van der Waals interactions. Unfortunately it is not possible to test this hypothesis with Hofer and Manes' theory, as the necessary data for Rhodamine WT is not available. Its application could however be attempted with rhodamine B, and fluorescein, the compositions of which are widely known.

It is significant that addition of water to the eluting alcohols produced considerable increase in the amount of dye desorbed. This cannot

be due to the low adsorption potential of water (Wohleber and Manes 1971) since that for the alcohol alone is smaller than for the mixture. It may, however, be due to competitive effects of the solvent and solute. Gasser and Kipling (1960) showed that the higher alcohols compete more effectively with benzene (solvent) at high concentrations than at low ones, when the lower more polar alcohols are more competitive. Dzhigit et al (1948) demonstrated that the maximum concentrations for adsorption of miscible alcohols from aqueous solution, decreased the greater the molar volume of the alcohol. This is in accord with the present findings, though the maximum concentrations are considerably different, perhaps due to the different carbons used.

In this study however, the effect is most easily explained with reference to the solubility of the dye. In methanol, which has small polar molecules most similar to water, the alcohol alone proves effective in giving high maximum fluorescence, as the dye is readily soluble in it. However, decreasing solubility in ethanol and the propanols, cause the optimum mixture to contain progressively more water, because increased solubility in general produces lower adsorption, and therefore more desorption, according to Lundelius' Rule (Hassler 1963 ch.2, Weber 1967). Once a given water content has been exceeded however, the decreased alcohol concentration lowers the amount of dye desorbed to produce a decline in fluorescence values. Although no solubility measurements have been made to test this hypothesis it is supported by the fact that 100% 1-butanol, which is sparingly soluble in water, releases no dye from carbon. However, if water is added then dye is rapidly desorbed - 1-butanol from solution is adsorbed on the carbon replacing dye, which goes into solution in the water. More butanol dissolves to replace that adsorbed

from solution. A similar process using chloroform was reported by Steenberg (1941) to elute methylene blue from charcoal.

Hamilton (1963 and 1966) has shown that the azeotropic mixture of two solvents provides the maximum extractive capability. It is probable that these are the optimum mixtures in this case also. Acetone and methanol do not form azeotropes (constant boiling point mixtures) with water, but the values for 1-propanol (56.8% water) and 2-propanol (31.5% water) are very close to the maximum in Fig. III:5. That for ethanol (10.6% water) does not show such good agreement. No explanation of this effect has been suggested by Hamilton. It might be fruitful to experiment with 1-propanol and 1,2-dichloropropane or 1,2-dichloroethane, (Hamilton pers. comm.).

The basic mechanisms of desorption have been discussed above but the effects of various inorganic additives have not been mentioned. The effect of pH on elution may be important as it can strongly change the solubility of weak electrolytes and therefore effect adsorption. For instance Rhodamine WT, if separated from its associated gegenion, can be precipitated in strong mineral acids, due to formation of the free molecular acid, which has low solubility. Highly soluble materials in general are poorly adsorbed, and therefore if conditions for adsorption correspond to those of maximum solubility, elution will be at a maximum. The effect of pH and ionic strength on adsorption of the dye have been discussed previously (p39); neither effect will be very important compared to solvent variation. The chief purpose of alkaline additives in elution is to produce optimum fluorescence of the solution, and cause complete dissociation of the dyestuff. Thus small amounts only are needed to produce pH values of approximately 9 for Rhodamine WT, 10 for rhodamine B and 12

Table III:5 Best Elutants for S Charcoal

Elutant (% by vol)	Maximum Fluorescence (Equiv. Fluor. Units)	Time to Maximum (mins)	Duration of Maximum (mins)
1% NH_4OH/EtOH*	92	30	20
99.2% EtOH	90	-	-
5% NH_4OH/EtOH*	186	20	50
95.7% EtOH	120	-	-
10% NH_4OH/EtOH*	245	30	60
91.4% EtOH	170	-	-
90% 1-PrOH	512	30	50
75% 1-PrOH	670	60	110+
50% 1-PrOH	850	80	90+
25% 1-PrOH	645	80	90+
75% 2-PrOH	490	120	120
50% 2-PrOH	610	80	220+
25% 2-PrOH	367	100	200+
75% EtOH	362	60	80+
50% EtOH	310	110	100+

\+ Decline from maximum did not occur before sampling ceased.

* % by weight.

for fluorescein (Feuerstein and Selleck 1963, Moser and Sagl 1967).

However it is apparent that ammonium hydroxide serves a dual purpose in elution; it stabilises fluorescence and augments desorption. The best elutants' properties, with respect to charcoal S, are shown in Table III:5. Values for ethanol of equivalent water content to the ammonium hydroxide samples are given below each appropriate reading. The effect of the ammonia is evident, it increases with concentration. It is generally recognised that ammonia is a readily adsorbed polar molecule,(Thorne and Ward 1939) which bonds onto polar functional groups. (Smišek and Černý 1970). Thus the results indicate that some desorption of dye by replacement on specific sites by the more polar compound ammonia does occur. Moloney and Findlay (1948) have used aqueous ammonia solutions to desorb insulin from charcoal, and Frieden (1944) describes the use of hot 5% aqueous ammonia for elution of folic acid from activated carbon. The additive has also been employed specifically for fluorescein and rhodamine B by Webb et al (1962) in toxicological studies of these dyes. Various alcohols were employed including methanol with 2.8% ammonium hydroxide in 80:20 ratio,and 1-butanol with 28% ammonium hydroxide in 98:2 ratio emulsion,to separate the dyes and their derivatives from faeces and bile.

The mineral acids and also potassium hydroxide give decreased desorption in relation to their respective pure solvents. This may be due partially to decay of the dye fluorescence due to conversion to the leuco-compound, but is probably also related to the increased ionic strength of the solution. The failure of acids to desorb the dye indicates that different adsorption mechanisms are operative for these and the dye. Dye adsorption is dominantly controlled by molecular size and by

hydrogen bonding, rather than specific ion - ion interactions related to its overall negative charge, as is the case for adsorption of acids (Mattson and Mark 1971 ch.6).

It thus appears that desorption of Rhodamine WT is dominated by replacement of dye, held by van der Waals forces at the carbon surface, due to competition from the alcohols. However, some dye is also released by strongly polar compounds, indicating that some specific bonds, probably hydrogen bonds, are also broken. The readsorption of dye which occurs during desorption appears to be contrary to any expectations. However the elutants used are unable to adsorb on the π bonding sites of the basal planes of the carbon skeleton, where no functional groups are present (Snoeyink and Weber 1967), as they do not have the requisite electron orbitals (Mattson and Mark 1971 p220). These are probably not populated by adsorbed dye until the higher bond strengths to polar sites have been satisfied. They therefore remain vacant and are available for readsorption of the dye released from polar functional groups on elution.

By employment of higher molecular weight secondary or tertiary alcohols e.g. glycerol and ethylene glycol, further desorption from van der Waals sites could occur, and blocking of readsorption sites would also be expected. An aromatic alcohol, for instance phenol, could cause desorption and blocking of the charge transfer sites on both π electron systems and surface oxide functional groups, and might therefore prove an excellent elutant. Further experimentation utilising these, now that the elution mechanisms have been explained, would be worthwhile.

C. Temperature

Two activated carbon samples were loaded with dye to give values

of 78µg/g (500ml 4.76 x 10^3 µg/l solution + 30g carbon for 24hrs) and 298µg/g (as for carbon W in Table III:2). They were washed in distilled water and dried in a natural convection oven at 115°C for 24hrs in thin layers. 1g samples were weighed into 60ml Pyrex-glass bottles with ground glass stoppers. These were warmed in a constant temperature water bath to the desired temperature and 20ml of 50% ethanol, at the same temperature was added from a pipette. Samples were taken at appropriate intervals using a prewarmed pipette and cuvette and their fluorescence determined on the fluorometer. Sample temperature was not measured as a suitable low mass probe was not available. Correction for change in fluorescence with temperature was made by determining the difference in reading for prepared samples at the elevated temperature and room temperature (21°C $\pm$ 1°C). All samples were returned to avoid appreciable volume loss. Sampling was discontinued when fluorescence declined from a maximum.

Water bath temperature was constant $\pm$ 1.0°C. Temperature values of 20, 30, 40, and 60°C were selected, the upper limit being set by the boiling point of ethanol (78.3°C). The experiment was replicated three times. The S samples had very poor homogeneity with respect to particle size; the runs at 20, 40 and 60°C were randomised but that at 30°C was added later and had appreciable smaller particle size than the others. This may explain its significant difference from the other results.

Fig. III:6 shows the effect of temperature of elutant on maximum fluorescence expressed as a mean ratio to that at 20°C. A good linear relationship is shown except for the 30°C run for carbon S. The S carbon uncorrected values indicate that visual detection will be decreased at high temperatures, due to the large decrease in fluorescence with

Fig. III:6 Effect of Elutant Temperature on Maximum Fluorescence

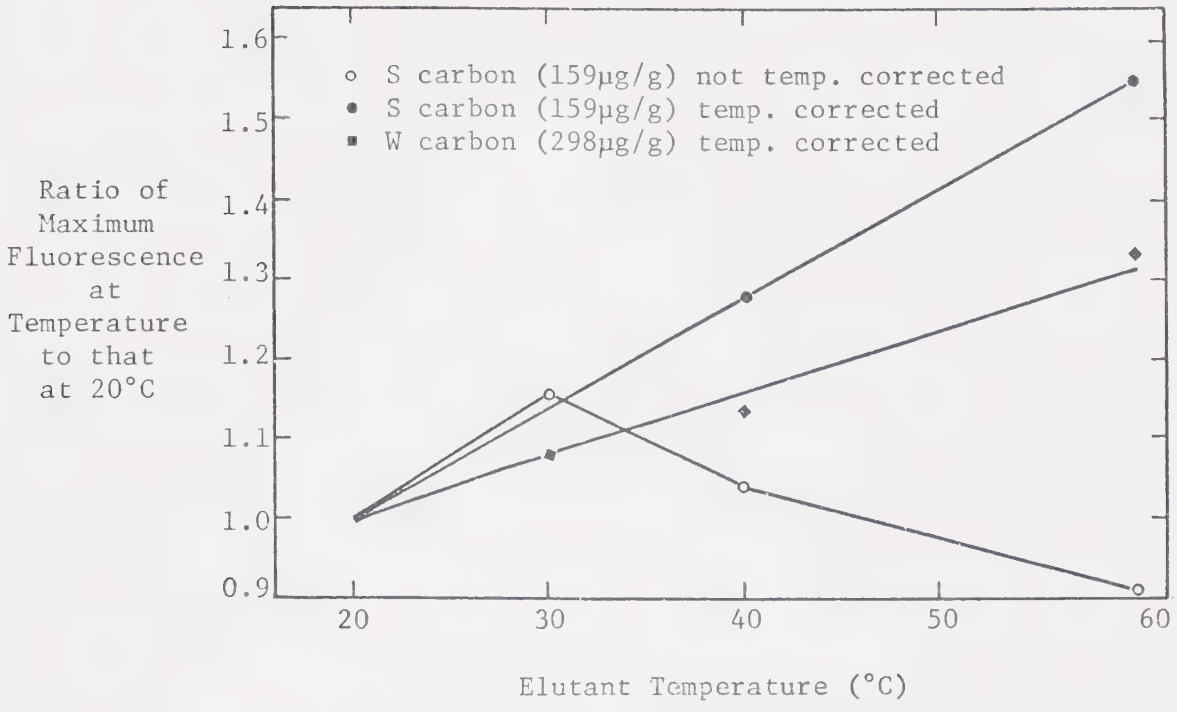
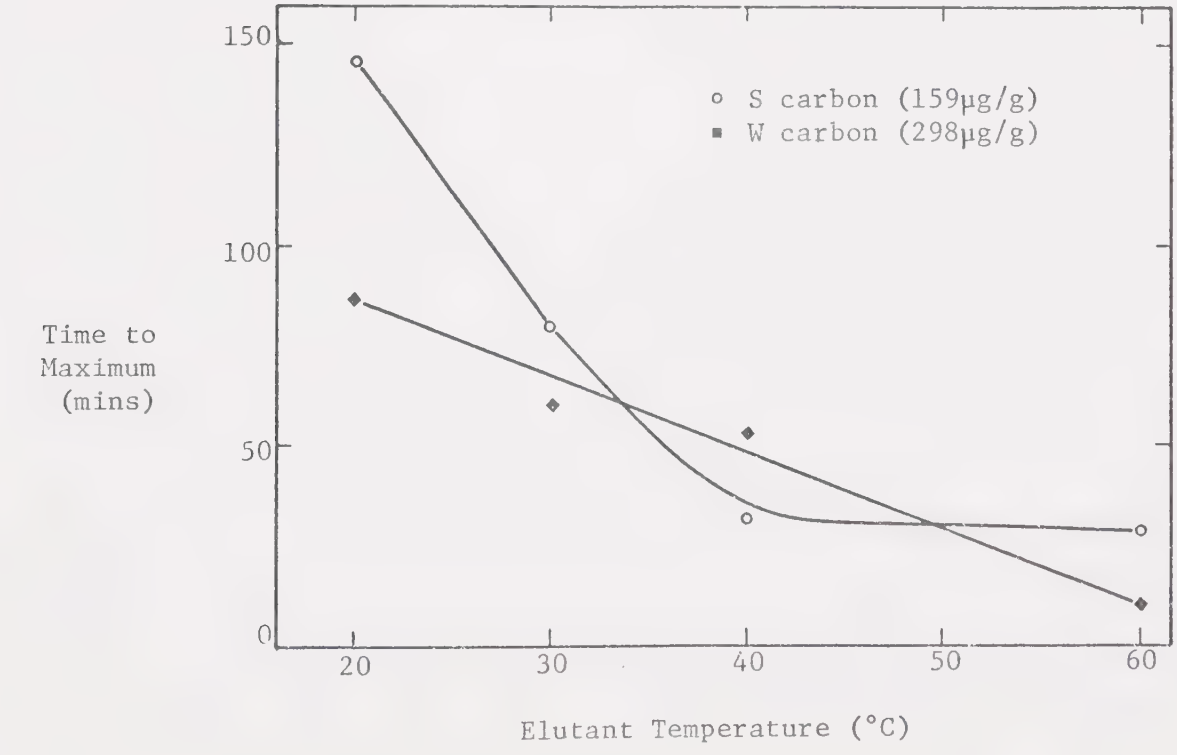


Fig. III:7 Effect of Elutant Temperature on Time to Maximum



temperature. Fig. III:7 presents the data relating time to maximum to temperature of elutant. A non-linear inverse relationship is shown for carbon S; the data for W indicates the same trend but the gradient is lower. No significant effect was observed for temperature on duration of maximum.

Although no data has been presented for this specific system, due to the exothermic nature of adsorption, increase in temperature will produce lower surface loading for a given concentration. (Weber 1967, Weber and Morris 1964b). This, coupled with the decrease in strength and specificity of van der Waals forces with temperature, which allows more alcohol to replace dye on the surface (Kipling 1965 p61), causes enhanced desorption at elevated temperatures. Leopold et al (1960) give an example of the release of 2,4-D, an aromatic acid, solely by increase in solution temperature from 21°C for adsorption to 95°C for desorption. However, more significant is the marked effect on the time to maximum. This is caused partially by the higher dye concentrations, which produce larger driving forces for readsorption and supression of desorption. However the major cause is change in the rate of internal transport which is a temperature sensitive diffusion process. (Smith et al 1959, Weber and Morris 1963a and Weber 1967). Consequently both dye release from the internal surface and dye readsorption are more rapid, though the latter may be slightly supressed. This produces a curve similar to that in Fig. III:4A. It is interesting that the effect on carbon with low dye loading (159μg/g) is less than that for a higher one (298μg/g). This, combined with the lower increase in maximum fluorescence, indicates that for low loadings insufficient dye is available at the surface to produce an equilibrium concentration. There must therefore be transport from internal

desorption sites into the solution; this is strongly temperature controlled. However with higher loadings (298µg/g) enough dye is available near the surface to produce an equilibrium concentration without necessity for intra-particle transport.

Thus the use of hot elutant will be advantageous for fluorometric detection in that it produces proportionally greater increase in concentration for samples of low loading than for higher ones, hence improving threshold levels. Furthermore it obviates the need for repeated sampling of the elutant concentration over periods of many hours to determine maximum concentration as time to maximum is drastically reduced at elevated temperature.

3. Dye/Carbon Interaction Effects

Data for this section has been derived from two sources; firstly the elution evaluation experiment (p71) and secondly from a specific set of samples prepared for the purpose. The former work suffers from the disadvantage that diffusion time, concentration and loading were varied simultaneously, so that the results cannot be used to illustrate the effect of one variable without noise from a second variable interfering. However the data gave a preliminary account of the effects expected in the latter experiments.

The second experiments were intended to be a factorial design with three factors; time since adsorption, loading, and initial concentration at four levels. However time did not permit the factorial design to be completed and hence a classical design, varying each factor individually while holding the others constant, was used. The levels employed were intended to represent those found in practical applications. They were

24 (standard), 73, 169, 330 and 504hrs for time since adsorption (subtract sixteen hours for actual adsorption process), 2.38×10^4, 2.38×10^3, 2.38×10^2 (standard) and 2.38×10 µg/l for initial concentration, and 20, 60, 95 (standard), 190, 280 and 380 µg/g for loading.

An appropriate weighed amount of 2.19mm carbon was contacted with a suitable volume of dye of desired concentration in a 1000ml beaker on a magnetic stirrer. After all the dye had been removed from solution the sample was removed from the stirrer and left to stand for the desired time period. It was then separated, washed in distilled water, and dried in thin layers at 115°C for twenty four hours in a natural convection oven. No noticeable effect on elution was found from this treatment compared to prolonged air drying at 21°C in thin layers. However, an increased residence period in the oven (91hrs) caused one third decrease in maximum fluorescence on elution. Two 0.5g samples of each batch of carbon were weighed into 60ml Pyrex-glass bottles with ground glass stoppers. Each bottle was placed in a water bath at 40°C to warm. 20ml of 75% ethanol with water at 40°C was added to each bottle and samples withdrawn with a warmed pipette into a cuvette for fluorometric determination of fluorescence at appropriate intervals. All samples were returned to avoid volume loss.

A. Loading

Fig. III:8 shows the effect of loading on maximum elutant fluorescence. The curve is essentially linear over two portions of different gradient. This suggests that the dye is held by two separate sites and/or mechanisms of different bond strength on the carbon surface. The steep portion of the curve represents the first occupied set of sites, which, despite strong affinity for the dye, release a large amount of

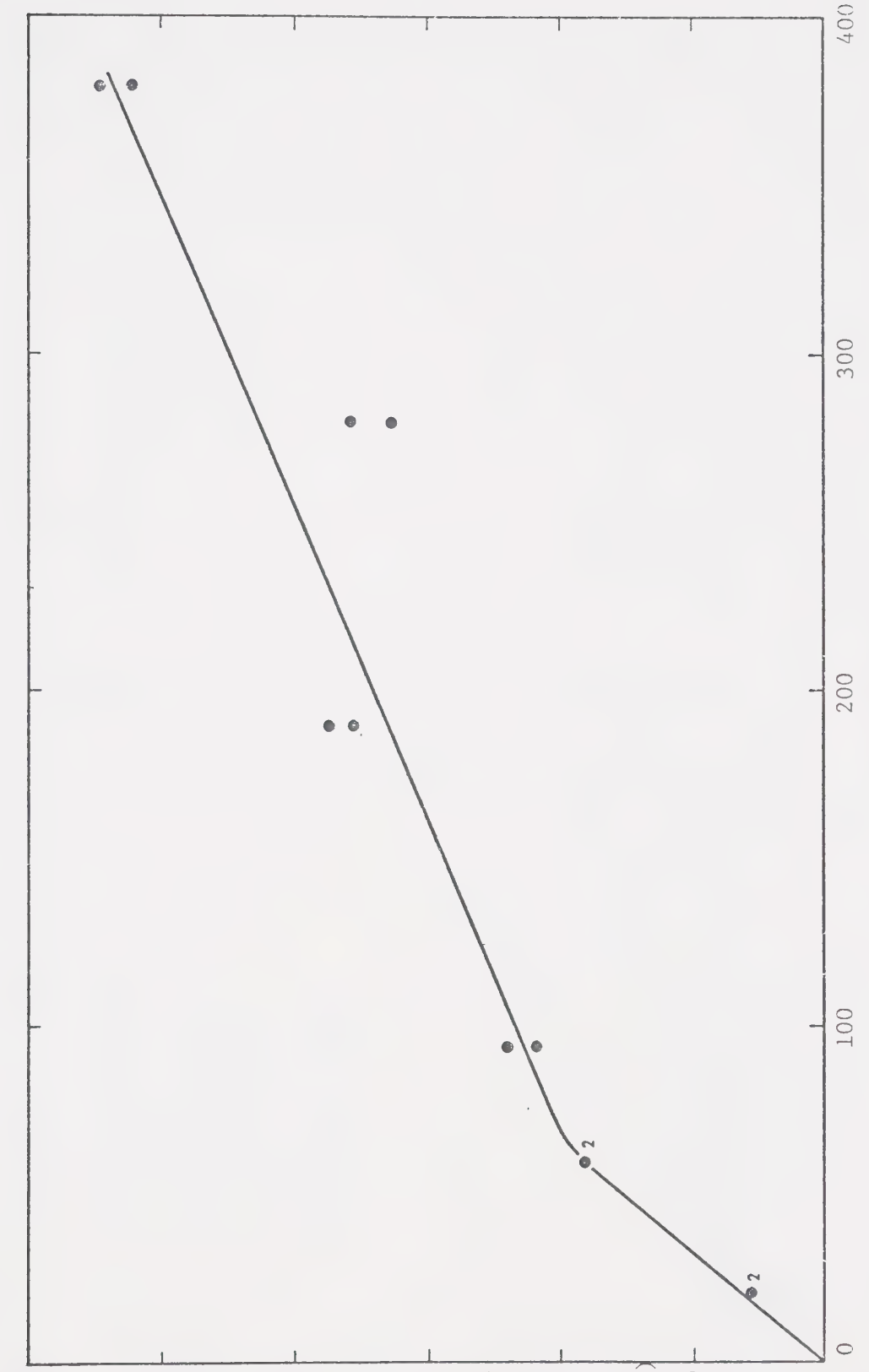


Fig. III:8 Effect of Loading on Maximum Fluorescence

Fig. III:9 Effect of Loading on Maximum Elutant Fluorescence

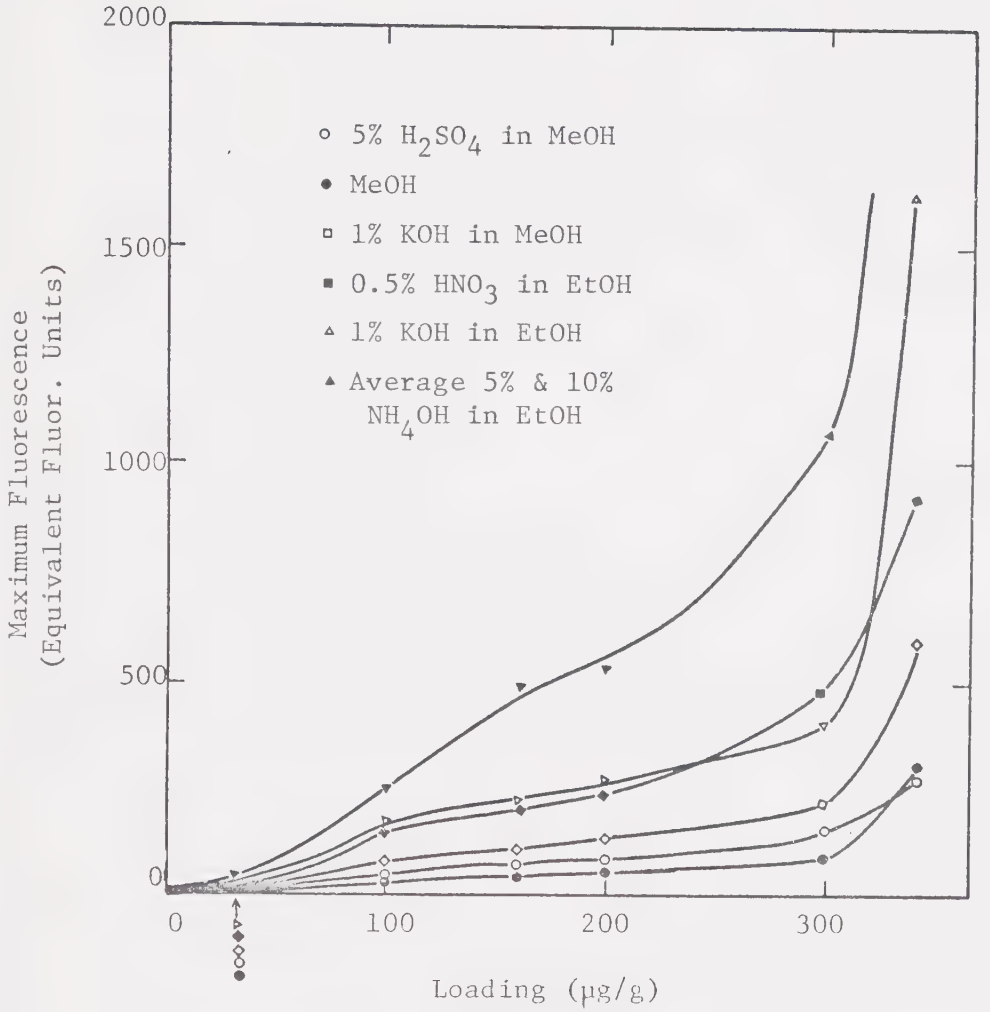
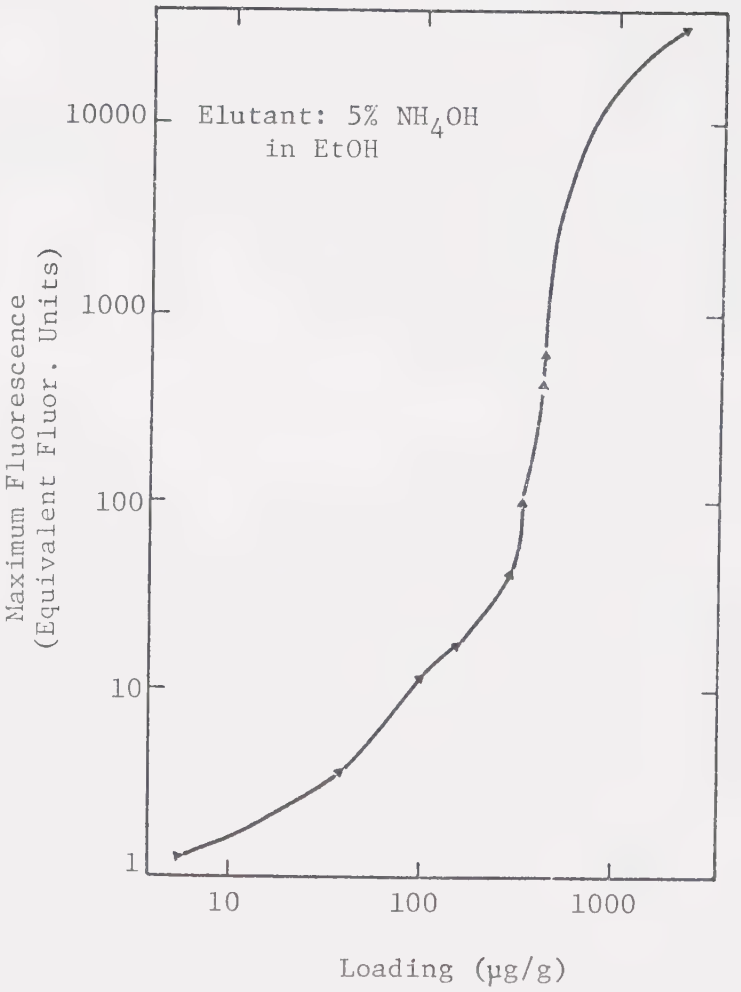


Fig. III:10 Effect of Loading on Maximum Fluorescence-High Range



dye on elution. The second portion of the curve represents a second series of sites, which although they have lower bond strength with the dye, are not eluted well by the alcohols and hence give a lower yield.

The elutant evaluation data shows similar steps (Fig. III:9) the one at 300µg/g being very marked, though having no apparent corresponding form in Fig. III:8. It is probable that the lower step, if any, is masked by the sample at 39µg/g which had a long diffusion time compared to the other points (Table III:2). These carbons were also prepared from initial solution concentrations one to two orders of magnitude higher than the ones in the above experiment, and this may have a considerable effect in that the critical micelle concentration is probably exceeded (Förester et al 1957). Thus micelles may be preferentially adsorbed as has been shown by Giles et al (1964), and a different adsorption mechanism may result, for which elution is highly efficient. Completion of the factorial layout would clarify these points.

Fig. III:10 shows a far higher range of loadings, using ethanolic 5% ammonium hydroxide elutant. It is evident that the steep gradient indicated in Fig. III:9 continues up to high loadings. This is predictable in that bond strengths for low loadings will tend to be far higher than those for greater ones (Graham 1959, Weber and Morris 1964b).

The data for time to maximum supports the argument presented earlier that low loadings are much more strongly controlled by intra-particle transport than higher ones (Fig. III:11). Hence longer times to maximum are shown for values below 100µg/g than above this value, where the time becomes nearly constant at 80 mins. Data from the elution evaluation runs do not show the initial maximum, probably because the higher concentrations used cause greater near surface adsorption, but the values

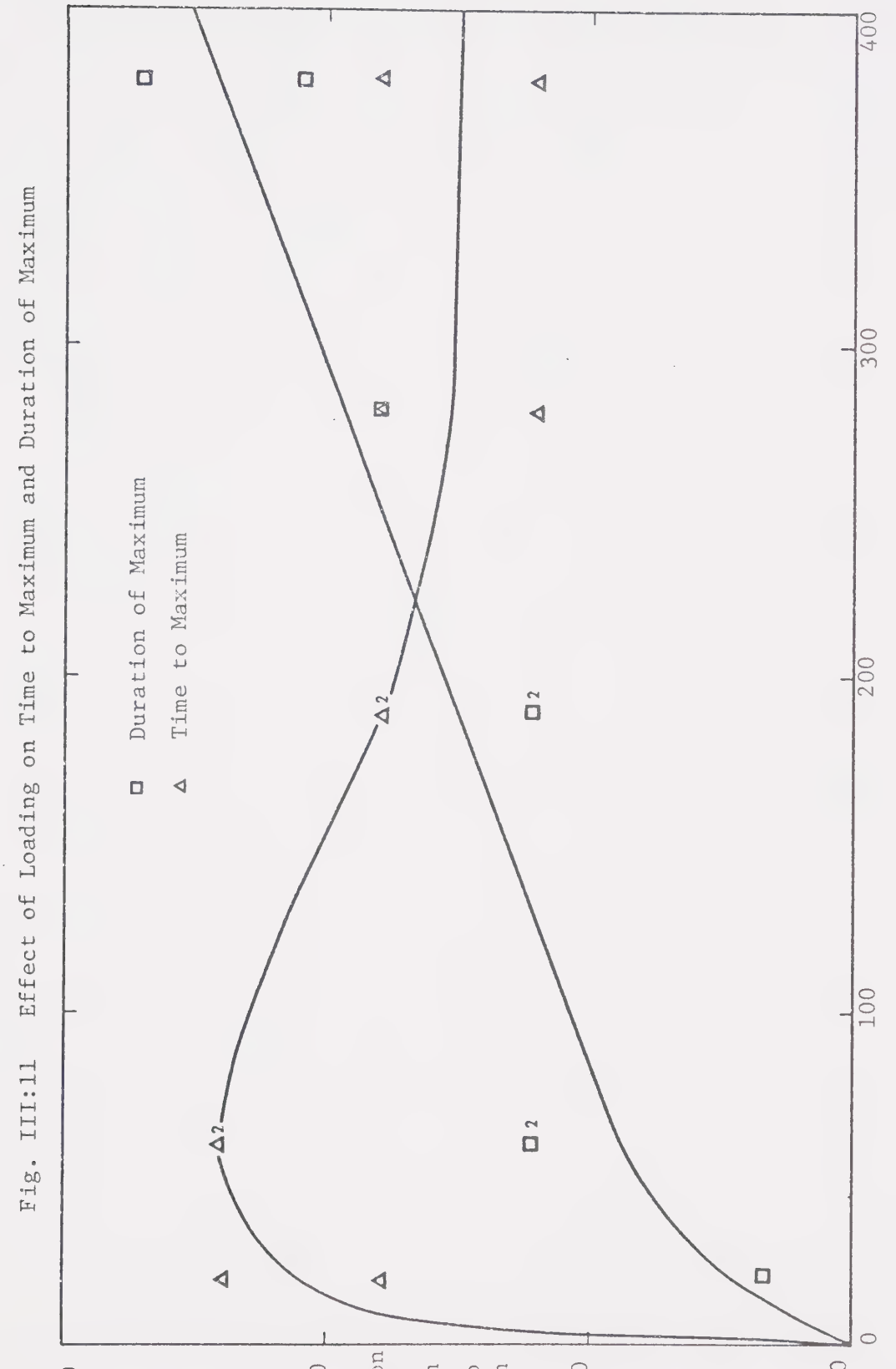


Fig. III:11 Effect of Loading on Time to Maximum and Duration of Maximum

are nearly constant above loadings of 100μg/g.

Fig. III:11 also shows duration of maximum, which increases with loading. Thus the decrease in availability of sites for readsorption, as higher surface coverage is achieved, decreases the rate of readsorption at a greater rate than increase in concentration elevates it, due to higher diffusion pressure. Furthermore, the higher loadings have more dye available for slow release, to maintain equilibrium concentration as dye is readsorbed, than the lower ones. The data from the elution evaluation runs is similar to that presented, but shows higher variance due to the variety of conditions used in carbon preparation.

Thus loading is of considerable importance in controlling elution, as is of course expected. However, it appears that simple linear calibrations between dye eluted and carbon loading cannot be made. Time since adsorption and concentration both appear to affect this calibration and must therefore be considered. This raises considerable difficulties in attempts to quantify the charcoal adsorption process. From the point of view of the threshold approach the non-linear loading/dye concentration is significant in that, for low initial concentrations, more dye is eluted for a given increase in loading than at higher ones. The process is therefore most sensitive in the threshold region, where it is most needed. However, the effect of lower dye concentrations on this relationship should be investigated.

B. Time Since Adsorption

The results of different times of adsorption on maximum fluorescence are shown in Fig. III:12. An initial decrease in maximum fluorescence occurred, but after 100 hours the values, although very variable, were

Fig. III:12 Effect of Time from Start of Adsorption on Fluorescence Maximum

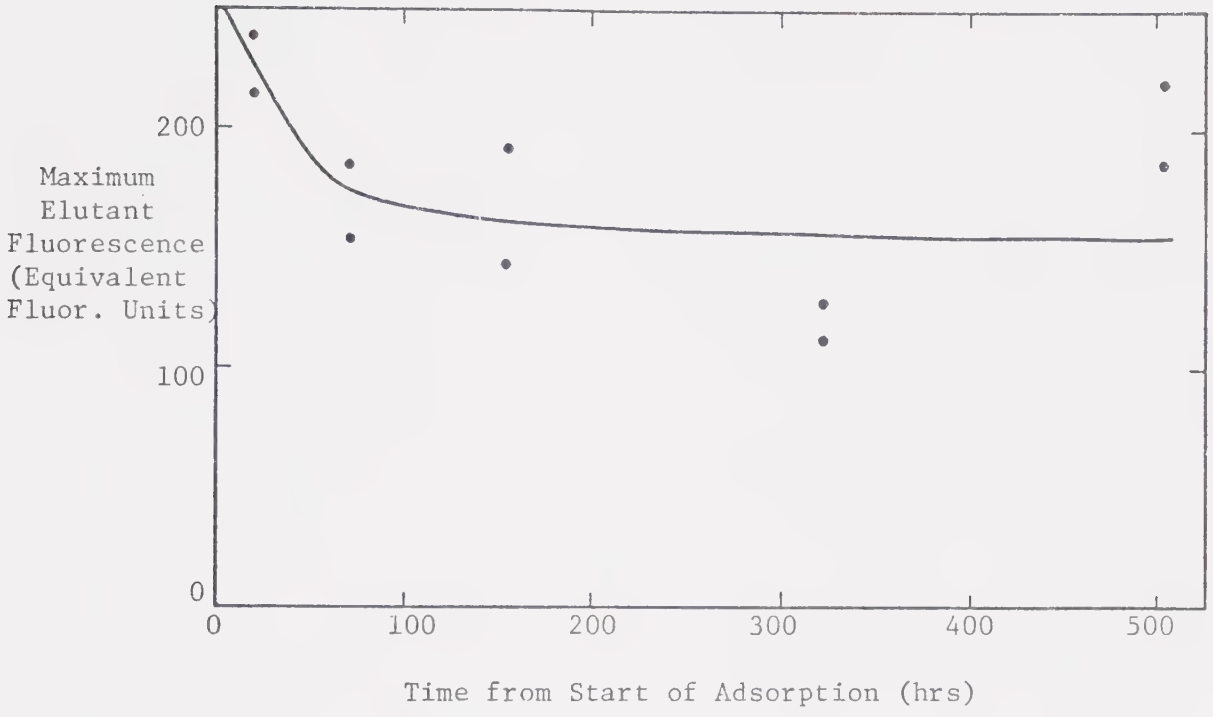
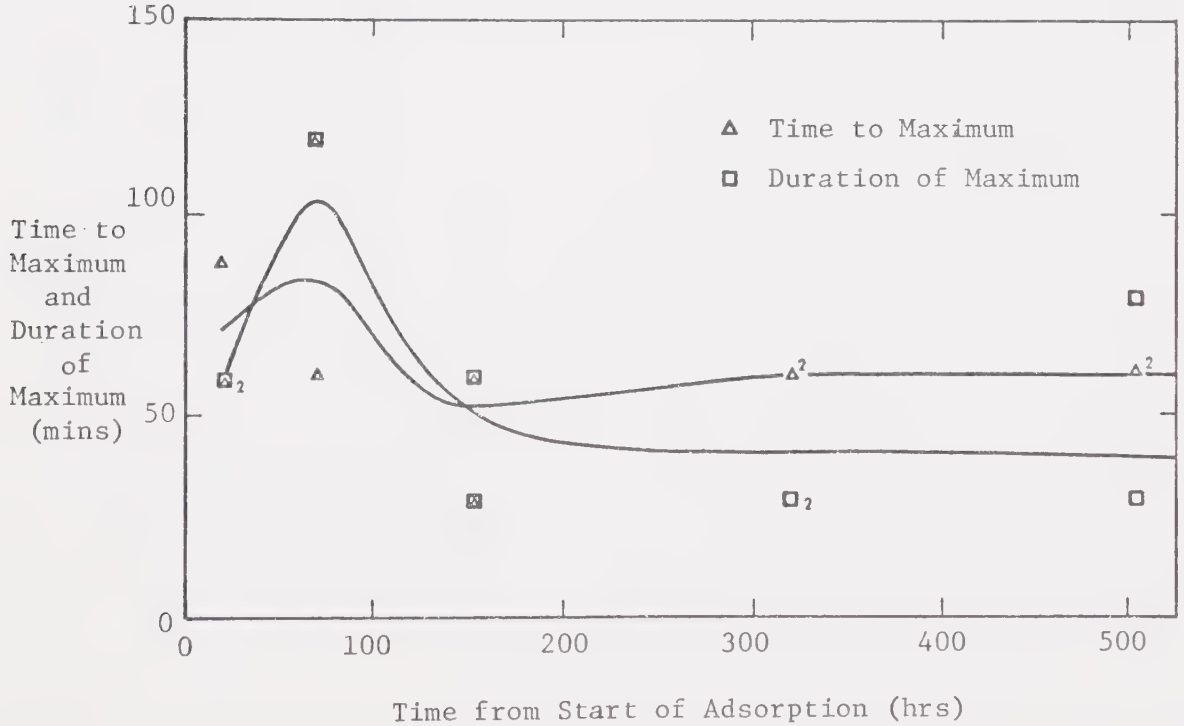


Fig. III:13 Effect of Time from Start of Adsorption on Time to Maximum and Duration of Maximum

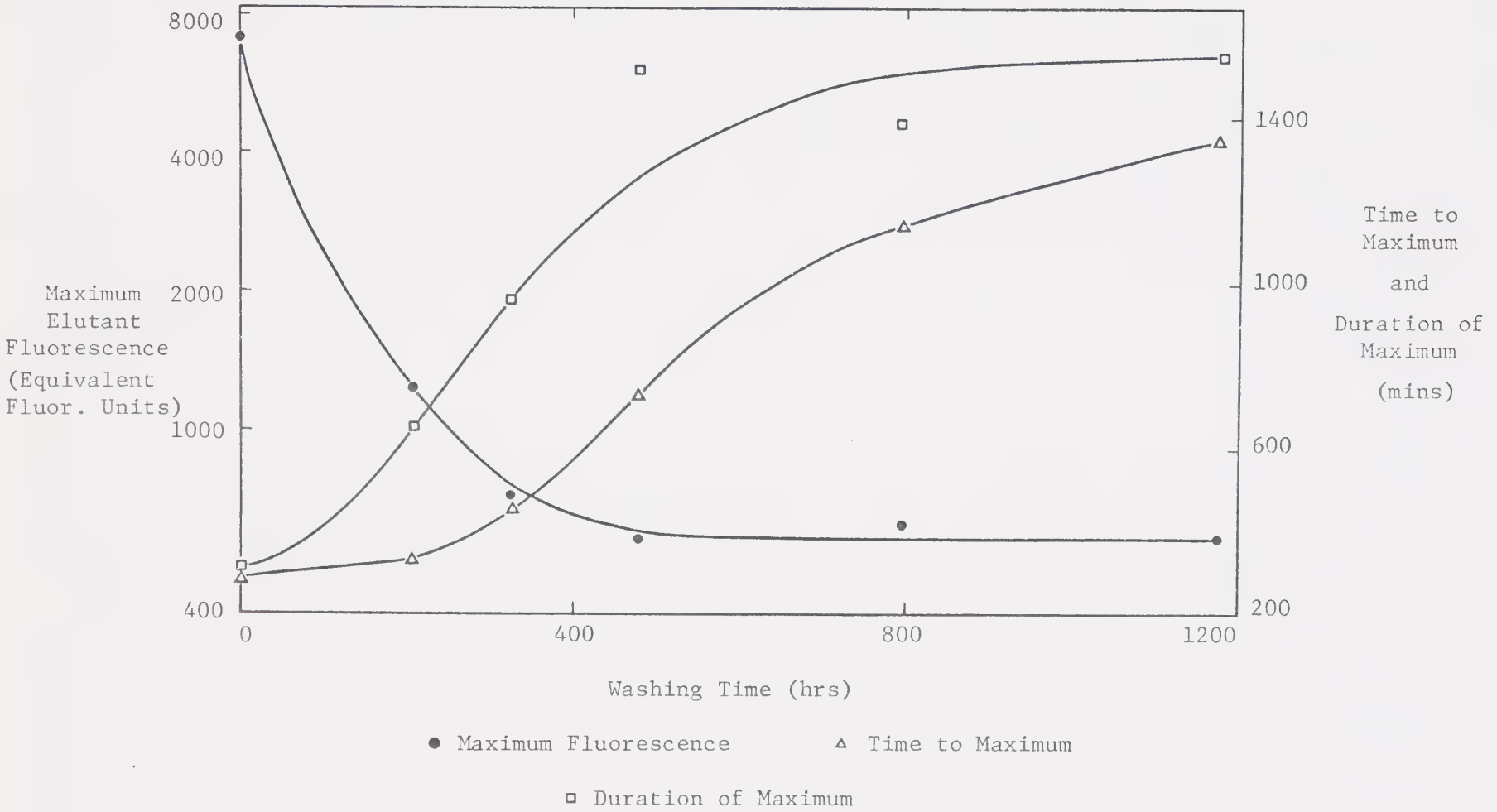


approximately unchanged. Both time to maximum and duration of maximum showed a small increase followed by a decrease to an almost constant level (Fig. III:13).

These results indicate that some relocation of the dye on the charcoal surface had occurred, and that the maximum effect had been within the first hundred hours. (Adsorption was complete within sixteen hours). The initial effect of relocation was to decrease fluorescence maximum and increase the time to maximum and duration of maximum, by decreasing the amount of dye available at the surface. However, further intra-particle transport, although not appreciably affecting the amount of dye now remaining at strongly bonded sites near the surface, prevented appreciable contribution by internal sites due to low coverage, while allowing readsorption to continue unaffected. Thus at low loading high average bond strength prevents diffusion.

A second experiment was conducted to assess this variable, using very much higher loading and a continuous flow situation. 20g of carbon were loaded with 1000ml of 4.76×10^4 µg/l dye solution. After 123hrs 5.84×10^3 µg/g remained. A loading of 2090 µg/g was therefore attained. The carbon was separated, washed in distilled water, and placed in a 250ml Pyrex-glass beaker. The outflow from a constant head tank was placed in the beaker, whose top was covered with a fifteen denier nylon mesh to prevent particle loss, but allow water to escape. The flow of tap water was adjusted such that the carbon was in continual motion in the beaker as water passed through. The flow varied between 1600 and 1400ml/min. At suitable periods 2g samples were removed from the beaker, washed in distilled water, and dried in thin layers in a natural convection oven at 115°C for 24hrs. All samples were stored in air tight vials

Fig. III:14 Effect of Washing Time on Maximum Fluorescence, Time to Maximum and Duration of Maximum



at room temperature until after completion of the washing part of the experiment. Two 0.1g samples of each batch were then weighed out into 60ml Pyrex-glass bottles, and 20ml of 75% ethanol in water was added. The elution was conducted in a water bath at 40°C. Samples were determined fluorometrically at appropriate time intervals until fluorescence declined from the maximum.

Fig. III:14 shows the results. The decrease in maximum fluorescence is of far greater magnitude in this case and the decline continues for 400 hours. Furthermore there is an increase in time to maximum of nearly three times, and of duration of maximum of five times over the 1200hr period of the run. The decrease in fluorescence maximum is caused by desorption (p 35) and migration of dye adsorbed on near surface sites further inside the carbon granule, where it becomes either inaccessible because of pore filling (Weber and Morris 1964a), or adsorbed on sites from which it is not readily removed. Similar effects due to internal transport have been noted by Weber and Morris (1963a) during work on adsorption of alkylbenzene sulphonates on activated carbon. If the carbon is removed from contact with the solution and left wet for a period of hours, considerable increase in adsorption rate occurs on replacing it; such an increase does not occur if the carbon is oven dried (Weber and Keinath 1967). Peterson and Lee (1971) show that such internal transport can also increase adsorption rates of rhodamine B on activated carbon.

The increase in both time to maximum and duration of maximum is due to the increasing dominance of internal desorption sites as diffusion continues. The high loading causes low bond strength adsorption sites to be utilised and hence the redistribution process has a considerably longer life than that in the previous experiment. The term internal

transport (Weber and Morris 1963b) has been used here, in that the forces governing intra-particle movement of molecules are not wholly those of diffusion - the driving force due to a concentration gradient. In addition adsorption and capillary forces are involved, such that the particle migrates from one site to another in a somewhat erratic manner. A mathematical treatment of this transport has been presented by Weber and Rumer (1965) which is based on a diffusion-with-adsorption form of Fick's Law.

A further experiment was conducted to show how continuous adsorption (field conditions) compares to the purely experimental batch techniques examined here. A low flow constant head apparatus was set using a very fine jet on the delivery tube. 800ml of 2.38×10^2 µg/l dye solution was placed in the apparatus, which had been previously adjusted to supply the 800ml volume over a period of 24hrs. The output was delivered to a 1000ml Pyrex-glass beaker on a magnetic stirrer, set to provide continuous suspension of the carbon particles. 2.5 g of sorted activated carbon was placed in the beaker in 200ml of dye solution to commence the experiment, the loading being 95 µg/g on completion of adsorption. The adsorption was complete after twenty five hours, the dye solution having been consumed after twenty four hours. The carbon was separated, washed in distilled water and dried in thin layers at 115°C for 24hrs in a natural convection oven. The samples were eluted in the same manner as those in the first time-of-adsorption experiment enabling the results to be compared with the 24hr sample from this run. The continuous input produced significantly higher maximum fluorescence on elution, slightly lower time to maximum and lower duration of maximum (See Table III:6). This was expected in that continuous input would leave considerable dye

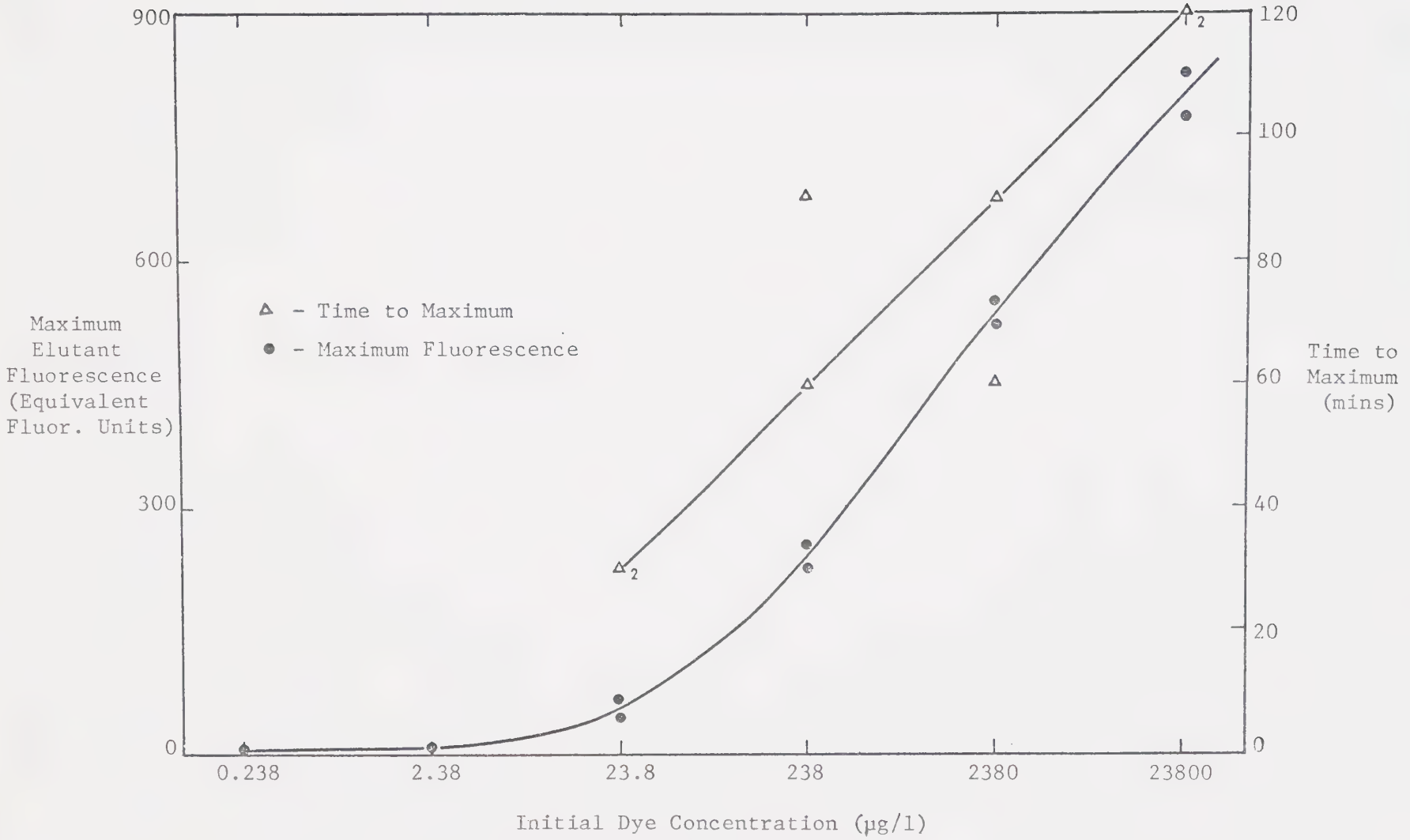
Table III:6 Comparison of Continuous and Batch Input Methods

	Maximum Fluorescence (Equiv. Fluor. Units)	Time to Maximum (mins)	Duration of Maximum (mins)
Continuous	184	60	0
	182	60	0
Batch	138	90	30
	120	60	30

on surface sites at the completion of the run, because time for transport to the internal surface was not available. However, in the batch system eight hours, during which no dye was adsorbed, were available solely for redistribution on the carbon surface. This difference also explains the time to maximum and duration of maximum results.

The influence of time since adsorption on maximum fluorescence is important in that it introduces considerable ambiguity into the maximum fluorescence/loading relationship. Furthermore neither time to maximum nor duration of maximum can give an estimate of its significance, as they are not appreciably altered at low loading. This considerably complicates any attempt to use the method for remote quantitative detection. A second important conclusion of this work is that if charcoal detectors are allowed to remain moist after collection, a reduction in elutant concentration will result, which could bring the level below the threshold value. A similar effect would be caused by long periods in the stream.

Fig. III:15 Effect of Initial Dye Concentration on Maximum Fluorescence and Time to Maximum



C. Initial Concentration

Fig. III:15 shows the results of variation of initial concentration on maximum fluorescence and time to maximum fluorescence. The points for concentrations below 2.38 x 10 µg/l were taken from a linear plot of the relationship. Data for duration of maximum fluorescence showed no significant variation. The values of maximum fluorescence are strongly controlled by solution concentration probably due to an increase in the average aggregation number of the adsorbed dye as higher initial concentrations are used (see p20). The use of ethanol as a solvent causes disaggregation of dye micelles (Giles et al 1964). Hence as more dye molecules are released by disaggregation of large micelles than of an equal number of small ones after release, the maximum elutant concentration is dependant on initial concentration. It is also possible that some dye/dye bonds may be broken without the micelle being desorbed from the surface, though this cannot be of great importance as a desorption mechanism because the higher alcohols give greater release than lower ones despite decreased polarity.

Adsorption from a solution of 2.38×10^4 µg/l is essentially complete within three hours at this loading, compared to eight hours for 2.38×10^3 µg/l and twenty four hours for 2.38 x 10 µg/l . Thus greater internal relocation may occur for the higher concentrations, especially in view of the high concentration gradients which are established. Thus time to maximum increases with concentration, though the amount is much more marked at low concentrations than at high.

It is apparent that changes in dye concentration are also significant in elution, and thus make quantitative interpretation of charcoal elution data indeterminate, in terms of dye loading on the carbon.

Furthermore, the effect is appreciable even at the low concentrations commonly used in dye tracing (a concentration of 2.38 x 10 µg/l is visible in deep water under good conditions, while fluorometric detection has a lower limit of 5×10^{-2} µg/l). Thus it is possible that for a given very low concentration, even if high loadings are achieved by prolonged adsorption, the dye may not be eluted. Continuation of the factorial design would have yielded useful information on this minimum concentration/loading interaction, which will be further modified by variation of the time since adsorption occurred.

IV CONCLUSIONS

1. Adsorption

1) Greater dye loading on the carbon will lead to higher maximum fluorescence of the elutant on elution. This relation is non-linear, indicating heterogeneity in adsorption sites, but the initial portion of the loading/maximum fluorescence curve has a steep gradient, giving maximum sensitivity in the threshold region. A variety of bond sites are present, the first ones being readily eluted, but strong, while those utilised at higher loadings are initially less readily eluted, but become progressively weaker and more easily eluted as loading increases.

2) The dye will be desorbed in water so as to adjust loading and/or solution concentration to equilibrium values. Hence desorption will occur in flowing water until a loading is achieved at which equilibrium concentration is just zero (zero concentration equilibrium loading). This indicates that van der Waals forces are responsible for dye adsorption, though a small amount of irreversible hydrogen bonding may operate on the sites occupied initially.

3) Zero concentration equilibrium loading increases with the concentration of the solution from which adsorption occurs. Furthermore, for a given loading, the maximum fluorescence of elutant on elution also increases with this variable. These effects are due to the adsorption of more larger dye micelles at high concentrations than at low ones.

4) Carbon capacity is not affected by large variations in pH,

ionic strength and probably temperature. However, in waters containing organic matter, either natural or effluent, competition for adsorption sites will occur and the carbon capacity will be reduced. This reduction is proportional to the flow rate through the detector and concentration of the organics. This competition is extremely important, because the organic matter will first utilise the high bonding energy sites, which are responsible for irreversible adsorption of dye. Thus dye may be adsorbed and desorbed again before analysis.

5) Intra-particle transport is the rate controlling mechanism in adsorption, except where rate of supply of dye is low. It may continue after adsorption has ceased, to either bring dye to the surface for desorption, if loading is above zero concentration equilibrium loading, or redistribute dye internally if the carbon is below this loading. The latter can continue as long as the detector remains moist, even if it is not submerged in water. This will result in decreased maximum fluorescence in solution, as little dye from deep internal sites contributes to maximum fluorescence on elution.

6) Adsorption rate is controlled by solution concentration and unused carbon capacity, which together provide the driving force in adsorption. At low loadings an increase in the carbon/dye weight ratio will increase adsorption rate, but this will also reduce loading, and is therefore undesirable.

7) Carbon capacity and rate of adsorption both increase with decreasing particle size; the latter is most significant. A relatively small particle size will increase the dye adsorbed from a unit volume of water passing the detector, but it will also be exhausted faster than

a large grain size of the same weight as more organic material will be adsorbed. Furthermore, desorption will also be more rapid.

8) pH, ionic strength and probably temperature do not significantly affect adsorption rates for the range of values expected in most fresh waters. However in waters of low pH and/or high ionic strength, adsorption rate is markedly increased due to supression of the negative charge on the carbon surface for the former and reduction in its effectiveness for the latter.

9) In waters containing competing organic molecules, adsorption rates are much lower than for pure distilled water systems. This is due to reduction in the rate of intra-particle transport due to pore blocking, inter-molecular repulsive forces, and reduction in the unused capacity of the carbon.

10) Due to the various effects of competing organics, solution concentration, desorption, rate of adsorption variations and of intra-particle redistribution of adsorbed molecules, it appears that adsorption on activated carbon cannot be used in quantitative applications to determine the mass of dye passed through a detector column with known flow.

11) The following recommendations on the use of detectors can therefore be made:

Dye concentration should be maintained at a maximum possible concentration (about 20μg/l) for as long as possible during a dye test. Continuous injection is therefore more satisfactory than slug injection. In streams with odorous or coloured waters, carbon capacity will be rapidly reduced. Detectors should therefore be changed frequently (every

one or two days). Even in relatively clean waters exposure for over periods of one week may drastically reduce the amount of dye adsorbed. Pipe or column detectors such as Dunn's original design or that of Bauer (1967) will be less severely affected by competition than screen ones, in that bed depth is finite and fresh carbon will be available at the outflow end of the detector.

Detectors should not be left in streams for long periods after dye adsorption, because desorption and redistribution will reduce the amount of dye which may be eluted. Similarly they should be dried on collection if analysis is not to be carried out immediately. Where short pulse durations or frequent detector replacement is expected (every day for instance), use of finer carbon (18-20 mesh) than the normal (6-14 mesh) will permit more dye to be adsorbed. However, for less frequent replacement (one week or more), the supplied size is more satisfactory. In order to ensure that rate of supply of dye does not become rate limiting, flow through the detector should be maximised. 12g of activated carbon is satisfactory for a 13 x 7cm screen detector, but larger quantities could be used in a column and eluted in several sequential portions.

2. Elution

1) Elutant flucrescence/time curves for the elution process pass through a maximum fluorescence value due to readsorption of the dye on the carbon.

2) The column elution system has an inherently higher minimum detectability than the batch, as the mass of dye released is larger, because elutant concentration does not limit desorption. However

concentration of the large volume of solution produced is needed and the procedure is generally more difficult.

3) The volume of elutant to weight of carbon ratio controls maximum fluorescence in batch elution; the smaller the ratio the higher the fluorescence obtained. Variations in volume or weight do not influence fluorescence for a given volume/weight ratio.

4) More dye is desorbed by high molecular weight alcohols than by low ones. For a given molecular weight, straight-chain alcohols are more successful than branched-chain ones. These findings indicate that desorption is due to competition for adsorption sites dominated by van der Waals forces.

5) With increasing molecular size, more desorption occurs with an increasing percentage of water in the elutant liquid. This is because the water increases the dye solubility in the elutant when the higher non-polar alcohols are used. For 1 and 2-propanol the optimum mixture is probably the azeotrope.

6) The use of ammonium hydroxide as an additive in elution causes release of some dye from polar adsorption sites, and also gives maximum fluorescence in the elutant. Other alkalis serve only the latter purpose.

7) Although increasing the temperature of elutant reduces the maximum elutant fluorescence, if temperature correction is applied for fluorometric detection the fluorescence does show a significant increase. More important is the decrease in the time to maximum fluorescence due to the increase in the rate of intra-particle transport from internal desorption sites to the bulk elutant with increasing temperature.

8) Thus the following may be recommended to optimise elution conditions:

The carbon weight used is unimportant, but the volume of elutant should be kept as small as possible, such that v/w is minimised. The elutant should be a mixture of 43% by volume 1-propanol and 57% by volume 20% aqueous ammonium hydroxide, at 60°C to 70°C if fluorometric detection is to be employed. This temperature should be maintained throughout the elution process using a water bath. A detectable concentration should be achieved within thirty minutes, for visual or fluorometric detection, if the carbon has a sufficient dye loading. Although maximum concentration may require considerably longer for samples which have high loadings, a visually detectable concentration will be reached rapidly. If a positive result has not been achieved it may be worthwhile, if the test is important, to use either a simple flow through system or repeated batch extraction with a short contact period, and concentrate the large volume of elutant. Extraction in a Soxhlet apparatus using the azeotropic mixture, would provide a continuous extraction and concentration process, which would prove more satisfactory than any other method.

The fluorescence of Rhodamine WT decreases rapidly above Cl^- concentrations of 0.01M, probably due to a specific reaction. The dye is less sensitive to $SO_4^=$, HCO_3^- and NO_3^- in that order. Fluorescence is not affected by pH above 8.5, is affected to a minor extent between 8.5 and 6.0 and decreases rapidly at lower values due to formation of the lactone form of the dye.

Work is under progress to test the findings of this study under field conditions, in order to develop specific methodological techniques for the use of carbon detectors. The work is also being extended to the use of sodium fluorescein and pyranine both of which are commonly used in water tracing work.

REFERENCES CITED

ALEY T. 1971 The Water Tracers Cookbook. Private publication.

ANDERSEN A.H. 1947 Experimental studies of the pharmacology of acitvated carbon. II The effect of pH on the adsorption by charcoal from solution. Acta. Pharmacol. 3, 199-218.

AMBROSE A.W. 1921 Underground conditions in oilfields. U.S. Bureau Mines Bull. 195, 106-120.

BAUCIC I. 1965 Subterranean connections in the hydrological drainage basin of the Cetina River. Proc. 4th Int. Spel. Cong. III, 271-277.

BAUER F. 1967 Erfahrungen beim Uraninnachweis mit Aktivkohle. Steirische Beiträge zur Hydrogeologie 1966/1967, 169-178.

BERGMANN K. and O'KONSKI C.T. 1963 A spectroscopic study of methylene blue monomer, dymer and complexes with montmorillonite. Journ. Phys. Chem. 67, 2169-2177.

BIDOVEC F. 1965 Investigations of the karst underground water systems and hydrology. Proc. 4th Int. Spel. Cong. III, 279-285.

BOEHM H.P. 1966 Chemical identification of surface groups. Advances in Catalysis 16, 179-279.

BROWN M.C. 1972 Karst geomorphology and hydrology of the lower Maligne basin, Jasper, Alberta. In press: Cave Studies.

BROWN M.C. and FORD D.C. 1971 Quantitative tracer methods for investigation of karst hydrologic systems. Trans. Cave Res. Grp. Gt. Britain 13, 37-51.

BROWN M.C., FORD D.C. and WIGLEY T.M.L., 1969 Water budget studies in karst aquifers. Journ. Hydrol. IX, 113-116.

BROWN M.C. and WIGLEY T.M.L. 1969 Simultaneous tracing and gauging to determine water budgets in inaccessible karst aquifers. In press: Proc. 5th Int. Cong. Spel.

BUCHANAN T.J. 1964 Time of travel of soluble contaminants in streams. Journ. San. Eng. Div. Am. Soc. Civ. Eng. 90:SAE3, 1-12.

CLARK W.M. 1925 Determination of Hydrogen Ions. Williams & Wilkins, Baltimore.

CLASSEN Von H.J. 1967 Der Einsatz von Färbeversuchen unter der Verwendung von Uranin im Untertagebetrieb des Tuhrberghaues und

seine Handhabung. Steirische Beiträge zur Hydrogeologie 1966/1967, 141-149.

COBB E.D. and BAILEY J.F. 1965 Measurement of Discharge by dye-dilution methods. Surface Water Techniques, Book 1, Ch.14. U.S. Geol. Surv.

COLLINS J.J. 1967 The LUB/equilibrium section concept for fixed-bed adsorption. Chem. Eng. Prog. Symp. Series no.74, v.63, 31-35.

CONN H.J. 1961 Biological Stains. 7th Ed. Williams & Wilkins, Baltimore.

COOKSON J.T. Jr. 1969 Mechanism of virus adsorption on activated carbon. Journ. Am. Water Works Assoc. 61, 52-56.

COUGHLIN R.W. 1969 Carbon as adsorbent and catalyst. Ind. Eng. Chem. Product Res. & Dev. 8, 12-23.

COUGHLIN R.W. and EZRA F.S. 1968 Role of surface acidity in the adsorption of organic pollutants on the surface of carbon. Journ. Env. Sci. Technol. 2, 291-297.

DAVIES R.A. 1968 The theory of selective adsorption on granular carbon. Die Stärke 8, 260-263.

DREW D.P. 1968 A review of the available methods for tracing underground waters. Proc. Brit. Spel. Assoc. 6, 1-19.

DREW D.P. 1968a Tracing percolation waters in karst areas. Trans. Cave Res. Grp. Gt. Britain 10, 107-114.

DREW D.P. and SMITH D.I. 1969 Techniques for the tracing of subterranean drainage. Brit. Geomorph. Res. Grp. Tech. Bull. 2, 36p.

DOLE R.B. 1906 Use of fluorescein in the study of underground waters. In Fuller M.C. U.S. Geol. Surv. Water Supply Paper 160. Underground water. 73-83.

DUNN J.R. 1957 Stream tracing. Mid Appalachian Region of National Spel. Soc. Bull. 2,7.

DZHIGIT O.M., KISELEV A.V., TEREKHOVA M.G. and SHCHERBAKOVA K.D. 1948 Adsorptive properties and the structure of adsorbents II. Adsorption by active carbon from solutions in a wide range of concentrations. Journ. Phys. Chem. U.S.S.R. 22, 107-20. Chemical Abstracts 42, 5298c (1948).

FEUERSTEIN D.L. and SELLECK R.E. 1963 Fluorescent tracers for dispersion measurements. Journ. San. Eng. Div. Am. Soc. Civ. Eng. 89: SA4, 1-21.

FÖRESTER T. and KÖNIG E. 1957 Adsorptionsspektren und Fluoreszenzeigenschaften konzentrierter Lösungen organischer Farbstoffe.

Zeit. Electrochem. 61, 344-348.

FRIEDEN E.H., MITCHELL M.K. and WILLIAMS R.J. 1944 Folic Acid II. Studies on adsorption. Journ. Am. Chem. Soc. 66, 269-271.

GALBRAITH J.W., GILES C.H., HALLIDAY A.G., HASSAN A.S.A., McALLISTER D.C., MACAULEY N. and MACMILLAN N.W. 1958 Adsorption at inorganic surfaces.III The mechanism of adsorption of organic solutes, including dyes, by graphite. Journ. Appl. Chem. 8, 416-424.

GARTEN V.A. and WEISS D.E. 1957 A new interpretation of the acidic and basic structures in carbons. Australian Journ Chem. 10, 309-328.

GARTEN V.A. and WEISS D.E. 1957a The ion and electron exchange properties on activated carbon in relation to its behaviour as a catalyst and adsorbent. Rev. Pure Appl. Chem. 7, 69-122.

GASSER C.G. and KIPLING J.J. 1960 Adsorption from liquid mixtures at solid surfaces. Journ. Phys. Chem. 64, 710-715.

GETZEN F.W. and WARD T.H. 1969 A model for the adsorption of weak electrolytes on solids as a function of pH. Journ. Colloid Interface Sci. 31, 441-453.

GILES C.H., EASTON I.A. and McKAY R.B. 1964 Mechanism of adsorption of cationic dyes by alumina and a note on heat changes in solution adsorption. Journ Chem. Soc. 1964, 4495-4503.

GILES C.H., EASTON I.A., McKAY R.B., PATEL C.C., SHAH N.B. and SMITH D. 1965 Association of adsorbed aromatic solutes. Trans. Faraday Soc. 62, 1963-1975.

GILES C.H. and D'SILVA A.P. 1969 Electro-kinetic and diffusion measurements of association of dyes in solution and adsorbed at solid surfaces. Trans. Faraday Soc. 65, 2516-2528.

GILES C.H. and D'SILVA A.P. 1969a Molecular sieve effects of powders towards dyes. Trans. Faraday Soc. 65, 1943-1951.

GRAHAM D. 1955 Characterisation of physical adsorption systems III. The separate effects of pore size and surface acidity upon the adsorbent capacities of activated carbons. Journ. Phys. Chem. 59, 896-900.

GRAHAM D. 1959 Adsorption equilibria. Chem. Eng. Prog. Symp. Series no.24 v.55, 17-23.

HAAS J.L. 1959 Evaluation of groundwater tracing methods used in speleology. Bull. Nat. Spel. Soc. 21, 67-76.

HAMILTON C.E. 1963 A new solvent system for improved extraction of activated carbon charcoal. Water & Sewage Works, 110, 422 -426.

HAMILTON C.E. 1966 A new twist to azeotropic distillation. Chem. Eng. Prog. 62, 92-94.

HANSEN R.S. and CRAIG R.P. 1954 The adsorption of aliphatic alcohols and acids from aqueous by non-porous carbons. Journ. Phys. Chem. 58, 211-215.

HASSLER J.W. 1963 Activated Carbon. Chem. Publishing Co., New York.

HASSLER J.W. and McMINN W.E. 1945 The nature of active carbon. Ind. Eng. Chem. 37, 645-649.

HECK E.T. 1954 Tracing fluids between wells. Producers Monthly 18, 31-33.

HOFER L.J.E. and MANES M. 1969 Adsorption on activated carbon from solvents of different refractive index. Chem. Eng. Prog. Symp. Series no.96 v.65, 84-88.

KÄSS W. 1967 Erfahrungen mit Uranin bei Färbuersuchen. Steirische Beiträge zur Hydrogeologie 1966/1967, 123-134.

KAUFMAN W.J. and ORLOB G.T. 1956 Measuring groundwater movement with radioactive and chemical tracers. Journ. Am. Water Works Assoc. 48, 559-572.

KILPATRICK F.A. 1970 Dosage requirements for slug injections of Rhodamine BA and WT dyes. U.S. Geol. Surv. Prof. Paper 700-B, B250-B253.

KIPLING J.J. 1965 Adsorption from Solutions of Non-Electrolytes. Academic Press, New York.

KIPLING J.J. 1967 Use of adsorption from solution in examining porous carbons. Chapter II in Porous Carbon Solids . Ed. Bond R.L., Academic Press, New York, 65-86.

KIPLING J.J. and WILSON R.B. 1960 Adsorption of methylene blue in the determination of surface areas. Journ. Appl. Chem. 10, 109-113.

KNOCKENMUS D.D. 1967 Tracer studies and background fluorescence of groundwater in the Ocala, Florida, area. U.S. Geol. Surv. Open File Rept.

KNUTSSON G. 1968 Tracers for groundwater investigations. In Groundwater Problems Ed. Eriksson E. Pergamon, London, 123-152.

LEE G.E., KUMKE G.W. and BECKER S.L. 1965 Recovery of organics from a eutropic lake by the carbon adsorption technique. Int. Journ. Air and Water Pollution 9, 69-80.

LEOPOLD A.C., VAN SCHAIK P. and NEAL M. 1960 Molecular structure and

herbicide adsorption. Weeds 8, 48-54.

LINDSTROM I.T., HAQUE R. and COSHOW W.R. 1970 Adsorption from solution III. A new model for the kinetics of adsorption-desorption processes. Journ. Phys. Chem. 74, 495-502.

MANES M. and HOFER L.J.E. 1969 Application of the Polanyi adsorption potential theory to adsorption from solution on activated carbon. Journ. Phys. Chem. 73, 584-590.

MARON S.H. and PRUTTON C.F. 1965 Principles of Physical Chemistry. 4th Ed. McMillan, London.

MATTSON J.S. and MARK H.B. Jr. 1971 Activated Carbon. Dekker, New York.

MOLITVIN P.V. 1966 Study of the relationship between surface and subsurface fissure-karst waters in the Ay River basin. Soviet Hydrology 1966, 557-567.

MOLONEY P.J. and FINDLAY D.M. 1924 Purification of insulin and similar substances by sorption on charcoal and subsequent recovery. Journ. Phys. Chem. 28, 402-406.

MOSER H. and SAGL H. 1967 Die Direktmessung hydrologischer Farbtracer im Gelände. Steirische Beiträge zur Hydrogeologie 1966/1967, 179-183.

PETERSON J.O. and LEE G.F. 1971 Sorption capacity estimation for activated carbon packed columns. Water Research 5, 717-721.

PLUMMER F.B. 1945 Tracing flow of fluids and gases beneath ground. Oil & Gas Journ. Sept. 29th 1945, p141.

PRATT L.S. 1947 Chemistry and Physics of Organic Pigments.

PRITCHARD D.W. and CARPENTER J.H. 1960 Measurements of turbulent diffusion in esturine and inshore waters. Bull. Int. Assoc. Sci. Hydrol. 20, 37-50.

REPLOGLE J.A., MYERS L.E. and BRUST K.J. 1966 Flow measurements with fluorescent tracers. Journ. Hydrol. Div. Am. Assoc. Civ. Eng. 92, HY5, 1-16.

SCANLAN J.W. 1968 Evaluation and Application of Dye Tracing in a Karst Terrain. Unpub. M.Sc. thesis, Univ. of Missouri-Rolla.

SMIŠEK M. and ČERNÝ S. 1970 Active Carbon - Manufacture, Properties and Applications. Elesevier.

SMITH S.B., HILTGEN A.X. and JUHOLA A.J. 1959 Kinetics of batch adsorption of dichlorophenol on activated carbon. Chem. Eng. Prog. Symp. Series no.24, v.55, 25-36.

SNOEYINK V.L. and WEBER W.J. 1967 The surface chemistry of active carbon: A discussion of structure and surface functional groups. Journ. Env. Sci. & Technol. 1, 228-234.

STEENBERG B. 1941 Naturwissenschaften 29:79.

STEENBERG B. 1944 Adsorption and Exchange of Ions on Activated Carbon. Almquist & Wiksells, Uppsala.

STURM P.W. and JOHNSON W.E. 1950 Field experiments with chemical tracers in flood waters. Producers Monthly December 1950, 11-17.

SWEARINGEN L.E. and DICKENSON B.N. 1932 The rate of adsorption from solution. Journ. Phys. Chem. 36, 534-545.

THORNE P.C.L. and WARD A.M. 1939 Inorganic Chemistry. Nordemann, New York.

UDENFRIEND S. 1962 Fluorescence Assay in Biology and Medicine. Academic Press, New York.

U.S. PATENT 3367946 (1968) Xanthene Dyes. U.S. Patent Office.

VELASCO J.R. and RUIZ J.O. 1945 Adsorption of dyes. Anales fís. y quím. 41, 1409-1428. Chemical Abstracts 42, 7129d, 1948.

VELASCO J.R. and RUIZ J.O. 1948 Adsorption in solutions V. Theoretical discussion of experimental results. Anales real. soc. espaň. fís. y quím. Ser. B 44, 69-94.

VICKERSTAFF T. 1954 The Physical Chemistry of Dyeing. Oliver & Boyd, London.

WATT J.P.C. 1965 Development of the Dye Dilution Method for Measuring Water Yields from Mountain Watersheds. Unpub. M.Sc. thesis, Colorado State Univ., Fort Collins, Colorado.

WARD T.M. and GETZEN F.W. 1970 Influence of pH on the adsorption of aromatic acids on activated carbon. Journ. Env. Sci. & Technol. 4, 64-67.

WEBB J.M., FONDA M. and BROUWER E.A. 1962 Metabolism and excretion patterns of fluorescein and certain halogenated fluorescein dyes in rats. Journ. Pharmacol. & Expt. Therapeutics 137, 141-147.

WEBER J.W. Jr. 1967 Sorption from solution by porous carbon. Proc. 4th Rudolph's Res. Conf., Principles of Applied Water Chem., Rutgers State Univ. 1965.

WEBER J.W. and KEINATH T.M. 1967 Mass transfer of perdurable pollutants from dilute aqueous solution in fluidised adsorbers. Chem. Eng. Prog. Symp. Series no.74 v.63, 79-89.

WEBER J.W. Jr. and MORRIS J.C. 1963a Kinetics of adsorption on carbon from solution. Journ. San. Eng. Div. Am. Soc. Civ. Eng. 89, SA2, 31-59.

WEBER J.W. Jr. and MORRIS J.C. 1963b Kinetics of adsorption from solution - closure. Journ. San. Eng. Div. Am. Soc. Civ. Eng. 89, SA6, 53-55.

WEBER J.W. Jr. and MORRIS J.C. 1964a Equilibria and capacities for adsorption on carbon. Journ. San. Eng. Div. Am. Soc. Civ. Eng. 90, SA3, 79-107.

WEBER J.W. Jr. and MORRIS J.C. 1964b Adsorption in heterogeneous aqueous systems. Journ. Am. Water Works Assoc. 56, 447-456.

WEBER J.W. Jr. and RUMER R.R. Jr. 1965 Intra-particle transport of sulphonated alkylbenzenes in a porous solid. Diffusion with non-linear adsorption. Water Res. Res. 1, 361-373.

WHITE W.B. 1967 Modifications of fluorescein dye groundwater tracing techniques. Steirische Beiträge zur Hydrogeologie 1966/1967, 151-158.

WHITE W.B. and SCHMIDT V.A. 1966 Hydrology of a karst area in East-Central West Virginia. Water Res. Res. 3, 549-560.

WILSON J.F. Jr. 1968a Fluorometric procedures for dye tracing. in Techniques of water resources investigations in the U.S. Geological Survey. Book 3, Chapter A12.

WILSON J.F. Jr. 1968b Time of travel measurements and other applications of dye tracing. Int. Assoc. Sci. Hydrol. Pub. no.76, 253-262.

WRIGHT R.R. and COLLINGS M.R. 1964 Application of fluorescent tracing techniques to hydrological studies. Journ. Am. Water Works Assoc. 56, 748-754.

ZOTTER H. 1963 Stream tracing techniques and results, Pochahontas and Greenbrier Counties, West Virginia. Nat. Spel. Soc. News. 21, 136-142.

——— * ———